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Characterization of PCB (Polychlorinated Biphenyl) Transformer/Capacitor Fluids and Correlation with PCDDs (Polychlorinated Dibenzo-p-dioxins) and PCDFs (Polychlorinated Dibenzofurans) in Soot

Technical Resources, Inc., Rockville, MD

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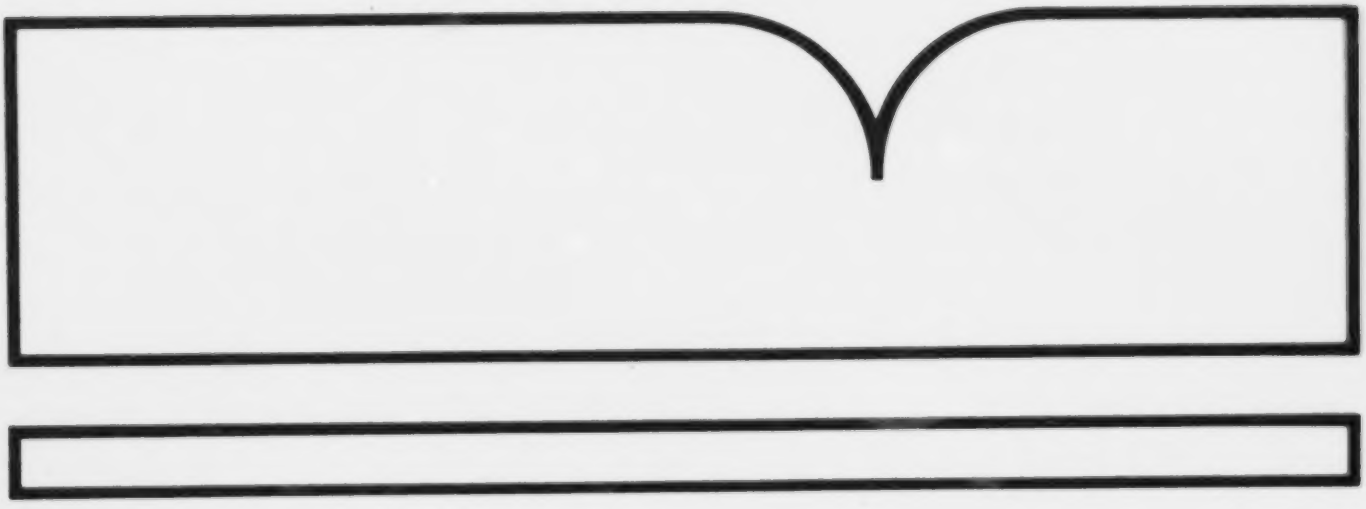

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CHARACTERIZATION OF PCB TRANSFORMER/CAPACITOR FLUIDS AND CORRELATION WITH PCDDs AND PCDFs IN SOOT

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16. ABSTRACT

Dielectric fluids in transformers and capacitors often contain polychlorinated biphenyls (PCBs) or chlorobenzenes. These substances may generate polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs) under certain conditions of combustion/pyrolysis. When electrical equipment containing these fluids is involved in an accidental fire, the resulting smoke, soot, and residues may be contaminated with PCDDs, PCDFs, and other toxic chlorinated hydrocarbons.

This report contains a review of several laboratory studies investigating the sources of PCDDs and PCDFs as well as the conditions under which they are formed. In addition, some data from sites of actual fire incidents are available and are discussed. Chlorobenzenes and PCBs do not form PCDDs and PCDFs when heated in the absence of oxygen. During fires the dielectric fluid of transformers or capacitors may be leaked or vented from ruptured casings. With exposure to oxygen, PCBs can produce PCDFs and chlorobenzenes can produce PCDDs. The particular isomers of PCDDs and PCDFs formed are related to the number of chlorine substituents in the reacting material.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs, and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small business in handling their wastes responsibly and economically.

This report describes the occurrence of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in residues following combustion or pyrolysis of dielectric fluids containing polychlorinated biphenyls (PCBs). Data from laboratory experiments and accidental fires involving electrical equipment have been evaluated to determine relative tendencies for different dielectric fluid compositions to produce PCDDs and PCDFs under combustion/pyrolysis conditions. The report will be useful to the electric utility industry, the owners and insurers of electrical equipment containing PCBs, emergency response personnel and organizations responsible for cleaning or disposing of contaminated material following a fire. For further information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

Thomas R. Hauser, Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

Dielectric fluids in transformers and capacitors often contain polychlorinated biphenyls (PCBs) or chlorobenzenes. These substances may generate polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs) under certain conditions of combustion/pyrolysis. When electrical equipment containing these fluids is involved in an accidental fire, the resulting smoke, soot, and residues may be contaminated with PCDDs, PCDFs, and other chlorinated hydrocarbons.

This report contains a review of several laboratory studies investigating the sources of PCDDs and PCDFs as well as the conditions under which they are formed. In addition, some data from sites of actual fire incidents are available and are discussed. Chlorobenzenes and PCBs do not form PCDDs and PCDFs when heated in the absence of oxygen. During fires, the dielectric fluid of transformers or capacitors may be leaked or vented from ruptured casings. With exposure to oxygen, PCBs can produce PCDFs and chlorobenzenes can produce PCDDs. The particular isomers of PCDDs and PCDFs formed are related to the number of chlorine substituents in the reacting material.

This report was prepared in fulfillment of Contract No. 68-03-3259 by **Technical Resources, Inc.**, Rockville, Maryland, under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from September 1985 to April 1986 and was completed as of May 1986.

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LIST OF ABBREVIATIONS

ABBREVIATIONS

ACGIH	--	American Conference of Governmental Industrial Hygienists
b.p.	--	boiling point
C	--	centigrade
CDD	--	chlorodibenzodioxin
CDF	--	chlorodibenzofuran
cm	--	centimeter(s)
cm^2	--	square centimeter(s)
d	--	day(s)
DCDD	--	dichlorodibenzodioxin
DiCDF	--	dichlorodibenzofuran
DOH	--	Department of Health
DRE	--	destruction and removal efficiency
EPA	--	Environmental Protection Agency
EPRI	--	Electric Power Research Institute
F	--	Fahrenheit
ft	--	foot or feet
g	--	gram(s)
gal	--	gallon(s)
GC/HRMS	--	gas chromatograph/high resolution mass spectrometer
GC/MS	--	gas chromatograph/mass spectrometer
HCCH	--	hexachlorocyclohexane
HpCBP	--	heptachlorobiphenylene
HpCDD	--	heptachlorodibenzodioxin
HpCDF	--	heptachlorodibenzofuran
hr	--	hour(s)
HRGC/MS	--	high resolution gas chromatograph/mass spectrometer
HxCBP	--	hexachlorobiphenylene
HxCDD	--	hexachlorodibenzodioxin
HxCDF	--	hexachlorodibenzofuran
IAFF	--	International Association of Fire Fighters
kg	--	kilogram(s)
L	--	liter(s)
lb	--	pound
m	--	meter(s)
m^2	--	square meter(s)
m^3	--	cubic meter(s)

ABBREVIATIONS

mcg	--	microgram(s)
mcl	--	microliter(s)
ml	--	milliliter(s)
m.p.	--	melting point
Mono-CDD	--	monochlorodibenzodioxin
Mono-CDF	--	monochlorodibenzofuran
MRI	--	Midwest Research Institute
NAPL	--	nonaqueous phase leachate
N.D.	--	not detected or none detected
ng	--	nanogram(s)
NIOSH	--	National Institute for Occupational Safety and Health
OCDD	--	octachlorodibenzodioxin
OCDF	--	octachlorodibenzofuran
PCB	--	polychlorinated biphenyl
PCBP	--	polychlorinated biphenylene
PCDD	--	polychlorinated dibenzodioxin
PCDF	--	polychlorinated dibenzofuran
PCDPE	--	polychlorinated diphenyl ether
PCP	--	pentachlorophenol
PCPY	--	polychlorinated pyrene
PeCDD	--	pentachlorodibenzodioxin
PeCDF	--	pentachlorodibenzofuran
pg	--	picogram(s)
PG&E	--	Pacific Gas & Electric Company
ppb	--	parts per billion
ppm	--	parts per million
PVC	--	polyvinyl chloride
TCDD	--	tetrachlorodibenzodioxin
TCDF	--	tetrachlorodibenzofuran
Tri-CDD	--	trichlorodibenzodioxin
Tri-CDF	--	trichlorodibenzofuran
TSCA	--	Toxic Substances Control Act
TWA	--	time-weighted average
wt	--	weight

SECTION 1

REGULATIONS PERTAINING TO PCBs, PCDDs, AND PCDFs

In August 1982, EPA decided to permit the continued use of electrical transformers containing polychlorinated biphenyls (PCBs) based on the reported low frequency of leaks and spills of PCBs from this equipment relative to the high costs of replacing or securing these transformers. Under Section 6(e)(2)(B) of the Toxic Substances Control Act (TSCA), EPA can authorize a use of PCBs provided that the use "will not present an unreasonable risk of injury to health or the environment." EPA determined that the continued use of PCBs-contaminated transformers (50-500 ppm PCBs), non-PCB transformers (< 50 ppm PCBs) do not present unreasonable risks to public health and the environment.(1)

A closer evaluation of the fire-related risks posed by the continued use of PCB transformers, and the costs and benefits of actions designed to reduce those risks followed the 1982 determination. EPA issued a Proposed Rule on October 11, 1984, concerning PCB transformer fires. EPA determined that fires involving transformers containing > 500 ppm PCBs present risks to human health and the environment.(2) The extreme toxicity of materials which can be formed during fires involving PCB transformers, and the potential for human and environmental exposures to these compounds, contributed to EPA's proposed rule.

EPA also determined that additional restrictions on the use of PCB transformers to reduce risk of injury to health and the environment were warranted. Therefore, EPA proposed additional regulatory controls(2) on the use of this equipment, requiring:

- The immediate registration of all PCB transformers with appropriate fire department jurisdictions, and the immediate registration with building owners of all PCB transformers located in or near buildings.
- The immediate marking of the exterior of the vault door, machinery room door, means of egress, or grate(s) accessing a PCB transformer with PCB identification labels.
- The immediate removal of stored combustibles from PCB transformer locations.

- The installation, by July 1, 1988, of additional electrical protective devices on PCB transformers in or near buildings in high secondary voltage systems (480/277 volt systems).

- The isolation, by July 1, 1988, of all PCB transformers in or near buildings from building ventilation systems, building ductwork, and openings in construction to reduce the widespread contamination of structures and the environment by smoke and soot in the event of a PCB transformer fire.

In order to facilitate monitoring compliance, EPA proposed that PCB transformer owners maintain records of their efforts in isolating transformers through the completion of PCB Smoke Spread Reduction Plans (PCB-SSRPs). EPA also proposed to require PCB transformer owners to take expedient measures to contain potential water discharges, and to report all PCB transformer fire incidents to the National Response Center before initiating cleanup efforts.

On consideration of the extensive comments received during the public comment period for the Proposed Rule, EPA modified the Final Rule concerning:

- Evaluation of the use of PCB transformers in or near industrial buildings separately from the use of PCB transformers in or near commercial buildings.

- Relative probabilities of failures and fires in different types of PCB transformers installations, placing more stringent controls on those transformers which EPA believes pose higher risks of failures and fires.

- Increased emphasis on the prevention of PCB transformer fires through increased electrical protection, and decreased emphasis on the use of isolation measures to minimize the spread of already formed and/or released contaminants.

On July 9, 1985, EPA promulgated its Final Rule on PCBs in electrical transformers, the culmination of a long fact-finding and rule-making process that began shortly after the transformer fire at the State Office Building in Binghamton, NY, February 5, 1981. This Final Rule states that PCBs at any concentration may be used in transformers (other than in railroad locomotives and self-propelled railroad cars) subject to the following conditions:

1) The use of higher secondary voltage ($\geq$ 480 volts) network PCB transformers in or near commercial buildings after October 1, 1990, is prohibited.

2) The installation of enhanced electrical protection on lower secondary voltage network PCB transformers and higher secondary voltage radial PCB transformers in use in or near commercial buildings is required by October 1, 1990.

3) Further installation of PCB transformers in or near commercial buildings is prohibited after October 1, 1985.

4) The registration of all PCB transformers with fire response personnel and building owners is required by December 1, 1985.

5) The marking of the exterior of all PCB transformer locations is required by December 1, 1985.

6) The removal of stored combustibles located near PCB transformers is required by December 1, 1985.

The Final Rule also requires that owners of PCB transformers involved in fire-related incidents immediately notify the National Response Center, and take measures as soon as practically and safely possible to contain any potential releases of PCBs or incomplete combustion products to water.(3)

This Final Rule does not spell the end of the issue surrounding PCB fluids in electrical equipment. Increased media coverage of the problem of toxic substances generation in electrical equipment fires has prompted increased public awareness. In Washington, D.C., recently, fires or leaks involving transformers in the Smithsonian Institution, the White House, and the Department of Health and Human Services received front-page attention in the Washington Post. Additionally, many utilities throughout the United States have hundreds of thousands of gallons of PCBs in storage awaiting proper disposal. As some utility companies have discovered, improper disposal can result in heavy penalties. In September 1985, the Potomac Electric Power Company (PEPCO) in Washington, D.C., signed a consent decree with the State of Maryland to clean up PCB contamination at a storage company to whom PEPCO sold 75 transformers contaminated with PCBs. The cleanup effort is expected to cost PEPCO from $1.5 to $3 million. Furthermore, the issue of PCBs-filled capacitors has not yet surfaced in the United States and it is not covered by the July 9 Final Rule. However, capacitor fires in Sweden and Finland have certainly drawn attention to this area as well; moreover, the recent transformer fire in Reims, France, has not dispelled this concern.

EPA has amended regulations for hazardous waste management under the Resource Conservation and Recovery Act (RCRA), by listing as acutely hazardous wastes certain wastes containing particular polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and chlorinated phenols, and by specifying management standards for these wastes.(4) The rule, promulgated January 14, 1985, defines certain waste streams as dioxins-contaminated wastes and thus, narrows waste treatment options to those approved for dioxins waste. EPA revoked the regulation (known as the "Vertac Rule") concerning the disposal of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) contaminated wastes under TSCA when the regulation under RCRA became effective on July 15, 1985.

This regulation proposes a degree of hazard approach for the dioxins-contaminated wastes which prohibits their management at most types of interim status facilities. Land disposal of these wastes must be conducted pursuant to additional special standards implemented during the course of the permit proceeding. Since all of these wastes are specifically identified as candidates for being banned from land disposal in two years under the Hazardous and Solid Waste Amendments (see RCRA amended Section 3004 (e)), EPA has proposed an interim regulatory regime for their land disposal.(5)

The only interim status facilities that are permitted to accept dioxins-contaminated wastes are:

- Impoundments holding wastewater treatment sludges that are created in these impoundments as part of the plant's wastewater treatment system.
- Waste piles that meet the requirements of Section 264.250 (c) referred to as "enclosed waste piles."
- Tanks, containers, and certified incinerators.
- Certified thermal treatment units subject to regulation under Subpart P of Part 265.

EPA may also issue emergency permits to facilities to store these wastes in situations where there is no other realistically available management capacity.

A waste management plan is required by EPA to ensure, as much as possible, that these wastes are properly managed in a land disposal situation. The plan will be the interim vehicle for assuring individualized consideration that the wastes will be managed safely. The waste management plan should address waste volume, concentrations of CDDs and CDFs in the waste aerosol/particulate dispersion, volatilization of the toxicants of concern, soil attenuation properties, waste leaching potential, and anticipated solvent co-disposal.

The Final Rule prohibits combustion of dioxins and furans contaminated wastes in incinerators that have only interim status. Interim status incinerators can burn these wastes without obtaining a RCRA permit if they are certified by the Assistant Administrator for Solid Waste and Emergency Response as satisfying RCRA standards for incinerators burning these wastes.

The hazardous waste regulations impose a more stringent destruction or removal efficiency (DRE) on incineration of CDDs and CDFs. The new DRE, 99.9999%, is technically feasible and has been measured at numerous incinerators.

This regulation defines RCRA acute hazardous wastes and subjects them to special standards when land disposed, incinerated, or stored. One part of the rule is intended to cover a broad variety of dioxins-contaminated wastes that are identified as EPA implements its Dioxin Strategy. In the implementation of this strategy, the Agency has established seven categories or tiers of investigation. Tier 4 covers: combustion sources such as municipal and hazardous waste incinerators, PCB transformer/capacitor fires, reactivation furnaces for spent granular activated carbon, boilers using PCBs and PCP-treated wood, etc.[6] Thus, this rule eventually may cover residue materials generated in a PCBs transformer fire if dioxins-contamination is determined, or, in situations where dioxins are found with "PCBs waste." A case in point is the problem encountered by a waste management company in Alabama. It accepted 40,000 gallons of "PCBs waste" from the Hyde Park Landfill in Niagara Falls, NY. Since the waste contained > 500 ppm PCBs, this waste was legally a PCBs waste. Unfortunately, Alabama State authorities were not informed via the forwarder's bill of lading that the nonaqueous phase leachate (NAPL) contained 20.2 ppm 2,3,7,8-TCDD along with hundreds of other

halogenated organic and pesticidal residues and substantial quantities (100 to 1,000 ppm) of toxic heavy metals. As a result, several of the 41 storage tanks at the waste management company's tank farm became contaminated with dioxin and 1.2 million gallons of PCBs wastes are now termed "dioxins wastes," with no short-term solution in sight.

U.S. regulations have focused on PCDDs and PCBs. To date, no Federal regulation has been promulgated specifically for PCDFs. However, if PCDDs or PCDFs are found in PCBs, disposal options for PCBs could be further restricted.

SECTION 2

SUMMARY AND CONCLUSIONS

An estimated 74,000 tons of PCBs are still in use in U.S. transformers and capacitors. On July 9, 1985, the EPA promulgated its Final Rule on PCBs in electrical transformers.[3] This rule specifies that PCBs at any concentration may be used in transformers (other than in railroad locomotives and self-propelled railroad cars) subject to the following conditions:

1) the use of higher secondary voltage (> 480 volts) network PCB transformers in or near commercial buildings after October 1, 1990, is prohibited.

2) the installation of enhanced electrical protection on lower secondary voltage network PCB transformers and higher secondary voltage radial PCB transformers in use in or near commercial buildings is required by October 1, 1990.

3) further installation of PCB transformers in or near commercial buildings is prohibited after October 1, 1985.

4) the registration of all PCB transformers with fire-response personnel and building owners is required by December 1, 1985.

5) the markings of the exterior of all PCB transformer locations is required by December 1, 1985.

6) the removal of stored combustibles located near PCB transformers is required by December 1, 1985.

There are still many uncertainties of the scope and nature of the hazards created in PCB transformer and capacitor fires. One potential hazard is the generation of highly toxic substances such as PCDDs and PCDFs from the pyrolysis of PCBs and chlorobenzenes. This report identifies 30 fire incidents involving PCB transformers and capacitors in the United States and western Europe, that occurred from September 1978 through February 1985. The following questions are addressed in this study:

- Are PCDDs and PCDFs formed in PCB transformers under normal operating conditions?
- How are the constituents of the transformer fluids related to the type and amount of PCDDs and PCDFs formed?
- What are the temperature and other reaction conditions that favor the formation of the PCB combustion products?

The July 9, 1985 rule provides for a gradual phaseout of some PCB transformers while recognizing the potential for additional fire accidents in the interim. Moreover, PCB capacitors are not covered under the July 9, 1985 rule and, since they have also been involved in fire incidents, capacitors are potential release sources for PCBs and combustion by-products into the environment.

This report presents and evaluates the available literature and published data on analyses of transformer fluids and soot generated in fires. Even though there have been at least 30 reported incidents, a wide variety of problems that hinder the analysis and evaluation of the data remain, including:

- Limitation of Analytical Data. Very few analytical data have been generated for each PCB fire incident. Because of the high cost of isomer analysis and the large number of isomers that characterize the PCBs, PCDFs, PCDDs, and PCBPs, few analyses are actually performed for any specific isomer in the aftermath of a PCB fire incident.

- Differences in Sampling and Analytical Protocols. Sampling and analysis protocols for contaminants generated in transformer fires are not yet fully standardized, and thus a wide variety of sampling and analytical methodologies are often employed. Some data are based on the analysis of soot and are reported on a weight/weight basis. Other data are based on the analysis of wipe samples and reported on a weight/area basis. Thus, it is very difficult to compare one fire incident with another, or to evaluate the significance of the data in one incident relative to that of another.

- Lack of Background Data. Very few background data are available on: (a) composition of transformer fluids and, (b) composition and levels of PCBs, PCDFs, chlorobenzenes, and PCDDs in the environment.

Despite these problems, the following conclusions may be made from analysis of the data from the literature on PCB transformer fires:

1) PCDFs and PCDDs are not formed in transformers containing PCBs under normal operating conditions. Their formation requires thermally stressful conditions and the presence of oxygen.

2) Electrical arcings in transformers do not lead to the formation of PCDFs and PCDDs.

3) A temperature zone between 600°C and 680°C may be regarded as optimal for the formation of PCDFs.

4) The amount and the specific PCDF isomers formed are related to the concentration of and type of PCB homologs in the transformer fluid.

5) Chlorobenzene diluents in the transformer fluids are required for the formation of PCDDs.

The Binghamton, NY transformer fire accident was the first to capture major media and scientific attention. In that fire, both PCDDs and PCDFs were found in the generated soot, leading to the concern that these compounds were being formed in situ in PCB transformers and capacitors under normal operating conditions. The available evidence does not support this concern. Analyses conducted by Electric Power Research Institute and EPA of samples of dielectric fluids taken from in-service transformers and capacitors and those involved in fire accidents showed no appreciable difference in PCDF values from stock material. No PCDDs were detected. Under normal use conditions, it does not appear that PCDFs are generated to any significant extent in the transformer.

Correspondingly, a second concern was whether PCDDs and PCDFs are formed during electrical discharges associated with transformer performance. To investigate this issue, experiments involving the arcing of electrical energy through various transformer fluids were performed. There was no appreciable difference in PCDF levels before and after electrical arcing. The supposition is that the level of oxygen is very low in the transformer and, thus, does not offer the environment for combustion resulting in the formation of PCDFs and PCDDs.

The amount and the specific PCDD and PCDF isomers formed in a PCB transformer fire appear to be related to the concentration of and type of PCB homologs in the transformer fluids. This supposition is supported by recent estimations on the boiling points for dioxins and furans that indicate that the boiling temperatures for tri-CDDs and tri-CDFs and the higher chlorinated PCDDs and PCDFs range from 375°C to 537°C. A first approximation of the thermodynamic conditions would favor the formation of tri- and higher chlorinated PCDFs and PCDDs. Combustion studies conducted by EPA and EPRI also provide evidence that the concentration of and type of PCB homologs in the transformer fluids are probably related to the amount and the specific PCDD and PCDF isomers formed in a PCB transformer fire.[7,8] The EPA study indicated that the optimal conditions for PCDF formation from PCBs are a temperature near

675°C and a residence time of 0.8 second or longer. The EPRI study demonstrated that tetra- and penta-CDF yields are roughly proportional to PCB concentrations in the starting material, but it indicated that significant dibenzofuran destruction begins to occur at approximately 550°C.(7,8)

A final issue pertains to the question of the use of diluents in transformer fluids. Of the 30 reported fire incidents involving PCB transformers and capacitors, unequivocal evidence of PCDDs formation was found only in the Binghamton, NY fire. The Binghamton, NY transformer contained chlorobenzenes as a diluent, adding to the evidence that the pyrolysis of chlorobenzenes leads to the formation of PCDDs. Such evidence has also been found in chemical manufacturing processes and in metal recovery sites involving PCB transformers. Chlorobenzenes should be carefully evaluated for use as transformer fluids or diluents.

SECTION 3

FIRE INCIDENTS INVOLVING PCB TRANSFORMERS AND CAPACITORS

PCBs have been used extensively as dielectric fluid in capacitors and transformers since the 1950s. An estimated 74,000 tons of PCBs are still in use in U.S. transformers and capacitors.[9] At least 30 fire incidents involving PCB transformers and capacitors have occurred in the past 7 years (Table 1). These fire incidents can be divided into three categories: (1) PCB fires with mineral oil as the external energy source; (2) PCB fires with electrical energy as the external energy source; and (3) explosions in PCB-filled capacitors. The following fires are discussed in more detail in this section:

- Binghamton, New York
- San Francisco, California
- Chicago, Illinois
- Cincinnati, Ohio
- Boston, Massachusetts
- Miami, Florida
- Columbus, Ohio
- St. Paul, Minnesota
- Norrtalje, Sweden
- Stockholm, Sweden
- Skövde, Sweden
- Surahammar, Sweden
- Imatra, Finland
- Hallstahammar, Sweden
- Railway Locomotive, Sweden
- Kisa, Sweden
- Reims, France
- Other Fires.

The finding of PCDFs and potential generation of PCDDs from askarels under thermal conditions may influence strategies for mitigating and controlling chlorinated dioxins and furans in the nation's environment. These PCB combustion products have complicated cleanup procedures for buildings having fires involving PCB transformers and capacitors. The analysis of soot samples from actual PCB transformer or capacitor fire incidents has indicated the presence of PCDFs, and, in at least two incidents, the presence of PCDDs.

Table 1. Fire Incidents Involving PCB Transformers or Capacitors Since 1978[9,10]

LOCATION	DATE
Norrtalje, Sweden	September 25, 1978
Cincinnati, Ohio	December 3, 1980
Binghamton, New York	February 5, 1981
Stockholm, Sweden	August 25, 1981
Danviken, Sweden	1981
Boston, Massachusetts	January 1982
Skövde, Sweden	March 19, 1982
Miami, Florida	April 13, 1982
Arvika, Sweden	May 1982
St. Paul, Minnesota	June 22, 1982
Imatra, Finland	August 3, 1982
Helsinki, Finland	August 1982
Surahammar, Sweden	September 23, 1982
Hallstahammar, Sweden	November 8, 1982
Railway Locomotive, Sweden	Winter 1982/83
Kaukopää, Sweden	1982
Kisa, Sweden	April 25, 1983
San Francisco, California	May 15, 1983
Halmstad, Sweden	August 15, 1983
Chicago, Illinois	September 28, 1983
Bofors, Sweden	December 21, 1983
Columbus, Ohio	March 1984
Södertälje, Sweden	April 27, 1984
Finspang, Sweden	May 24, 1984
Hofors, Sweden	September 13, 1984
Vetlanda, Sweden	October 10, 1984
Reims, France	January 14, 1985
Oslo Lysverker, Norway	January 1985
Sandnes, Norway	February 1985
Raufoss, Norway	February 1985

Binghamton, New York

On February 5, 1981, a fire broke out in the basement mechanical room of the 18-story State Office Building in Binghamton, New York. The switchgear in the mechanical room was located adjacent to two electrical transformers filled with 1,060 gallons of Pyranol, a nonflammable insulating oil. Electrical arcing from the switchgear ignited insulation around one of the transformers. Several explosions were heard from the machine room and, before the electrical power could be switched off, it was obvious that the fire had affected the transformer. The heat from the fire cracked a ceramic bushing on one of the transformers and approximately 180 gallons of Pyranol (65% Aroclor 1254 and 35% chlorinated benzenes) sprayed onto the floor and into the hot switchgear.

Immediately following the fire and before the extent and nature of the contamination was known, more than 300 people reentered the building to help with the cleanup or to retrieve documents and personal effects. Over $1 billion in lawsuits have been filed in the names of 23 individuals and groups against the state, most filed by fire fighters. Some 500 people who believe they were exposed are being monitored.

The New York Office of General Services began an immediate cleanup of the building. Members of the cleanup crew developed skin rashes and on February 26, cleanup was halted when the presence of PCDFs and PCDDs was discovered. Analysis of soot samples recovered from the building revealed high concentrations of PCBs and the presence of ten different polychlorinated dibenzofurans, dibenzo-p-dioxins, and biphenylenes at lower concentrations. PCBs, 2,3,7,8-TCDD, and 2,3,7,8-TCDF were found throughout the building. Analysis results are summarized in Tables 2 and 3. The total PCDF concentrations in the soot were initially reported to be as high as 2,163 ppm, PCDDs 10-20 ppm, and PCBs 100,000-200,000 ppm.[11,12,13,14]

Solid waste disposal from the site had reached a total of 4,676 cubic yards of material by February 1985. This material filled 1,464 barrels which were buried in an approved secure landfill site. All of the furniture in the building was removed, destroyed and buried, and will have to be replaced.

Table 2. Concentrations of PCBs, PCDDs, and PCDFs Found at Binghamton State Office Building Prior to Cleanup[11,12]

SAMPLE LOCATION	TYPE OF SAMPLE	CHEMICAL	CONCENTRATION(AVERAGE)
Composite (throughout building)	Air	PCBs	1.48 mcg/m^3
Composite	Air	2,3,7,8-TCDD	0.3 ppm
Composite	Air	2,3,7,8-TCDF	21 ppm
Composite	Soot	2,3,7,8-TCDD	3.5 ppm
Composite	Soot	2,3,7,8-TCDF	200 ppm
4th and 7th floor	Soot	2,3,7,8-TCDD	2-5 ppm
4th and 7th floor	Soot	2,3,7,8-TCDF	300 ppm
Air ducts	Soot	PCBs	156-1200 mcg/m^2
Interstitial space above ceiling levels	Soot	PCBs	1995 mcg/m^2
Exposed horizontal surfaces (desk tops, floors, sills)	Soot	PCBs	162.18 mcg/m^2
Exposed vertical surfaces (walls, desk sides)	Soot	PCBs	6.76 mcg/m^2
Unexposed horizontal surfaces (inside closed file cabinets and desk drawers)	Soot	PCBs	74.47 mcg/m^2
Unexposed vertical surfaces (inside closed cabinets and drawers)	Soot	PCBs	4.62 mcg/m^2
Garage and sub-basement floors and surface areas	Soot (swab)	PCBs	0.61 mcg/m^2

Table 3. Levels of PCDFs and PCDDs in Soot from Accidental Burning of PCB-Containing Electrical Equipment at Binghamton[13,14]

ISOMERS	AMOUNT (ppm)
Total PCDFs	2163
Total Tri-CDFs	--
Total Tetra-CDFs	28
2,3,7,8-Tetra-CDF	12
Other Tetra-CDF Isomers (6)	16
Total Penta-CDFs	670
1,3,4,7,8-Penta-CDF	65
1,2,4,7,8-Penta-CDF	25
1,2,4,7,9-Penta-CDF	22
1,2,3,7,8-Penta-CDF	310
1,2,3,6,7-Penta-CDF	60
1,2,6,7,8-Penta-CDF	25
2,3,4,7,8-Penta-CDF	48
2,3,4,6,7-Penta-CDF	12
Other Penta-CDF Isomers (12)	110
Total Hexa-CDFs	965
1,2,3,4,6,8-Hexa-CDF	50
1,3,4,6,7,8-Hexa-CDF	125
1,2,4,6,7,8-Hexa-CDF	50
1,2,3,4,7,8-Hexa-CDF	510
1,2,3,6,7,8-Hexa-CDF	150
1,2,3,6,8,9-Hexa-CDF	58
2,3,4,6,7,8-Hexa-CDF	10
Other Hexa-CDF Isomers	250
Total Hepta-CDFs	460
1,2,3,4,6,7,8-Hepta-CDF	230
1,2,3,4,6,7,9-Hepta-CDF	120
1,2,3,4,6,8,9-Hepta-CDF	55
1,2,3,4,7,8,9-Hepta-CDF	55
Octa-CDF	40
Total PCDDs	20
Total Tri-CDDs	--
Total Tetra-CDDs	1.2
2,3,7,8-Tetra-CDD	0.6
Other Tetra-CDD Isomers (4)	0.6

Table 3. Levels of PCDFs and PCDDs in Soot from Accidental Burning of PCB-Containing Electrical Equipment at Binghamton (Continued)

ISOMERS	AMOUNT (ppm)
Total Penta-CDDs	5.0
1,2,3,7,8-Penta-CDD	2.5
Other Penta-CDD Isomers (7)	2.5
Total Hexa-CDDs	4.7
1,2,3,4,6,8-Hexa-CDD	1.2
1,2,4,6,8,9-Hexa-CDD	1.2
1,2,3,4,7,8-Hexa-CDD	0.7
1,2,3,6,8,9-Hexa-CDD	0.6
1,2,3,7,8,9-Hexa-CDD	0.4
1,2,3,4,6,7-Hexa-CDD	0.5
Total Hepta-CDDs	7
1,2,3,4,6,7,9-Hepta-CDD	4
1,2,3,4,6,7,8-Hepta-CDD	3
Octa-CDD	2

The building is scheduled to be reopened during the summer of 1986, by which time the cost of the cleaning operation is estimated at close to $22 million, which exceeds the building's original cost of $20 million. Estimates of the cost of tearing down the building, safely disposing of the contaminated materials, and erecting a replacement building, reached as high as $100 million.

Reoccupancy of the building is based on an exposure assessment carried out by the Bureau of Toxic Substance Assessment of the New York State Department of Health. The contamination cleanup criteria established by the expert advisory panel was 10 pg/m^3 of 2,3,7,8-TCDD equivalents in the air of the building, and 3 pg/m^2 of 2,3,7,8-TCDD equivalents present on surfaces.[15]

San Francisco, California

On the morning of Sunday, May 15, 1983, an electrical fire of unknown origin occurred in an underground transformer vault located at One Market Plaza in San Francisco adjacent to a 28-story high-rise. The vault, located beneath a sidewalk manhole grate, contained three Pacific Gas and Electric Company (PG&E) transformers and associated network protection equipment. Each of the three transformers was filled with approximately 515 gallons of PCB fluid (100% Aroclor 1242).

During the course of the fire, a cooling fin on one of the transformers was damaged, resulting in the release of approximately 50 gallons of PCB fluid. The fire burned and smoldered for approximately 8 hours after discovery. Subsequent sampling of the building and surrounding area indicated that PCBs and by-products of PCB combustion had been released through the side- walk grate, through conduits into the building's switchgear room, and through discontinuities in the vault wall into an adjacent basement garage. The ventilation system serving floors B-2 through 6, which draws air from a point near the switchgear room, was also shown to have surface contamination of PCBs and combustion by-products.

Samples taken and analyzed after the incident revealed that the transformer oil involved was 100% Aroclor 1242 and contained no chlorobenzenes. Sampling for PCBs and tetrachlorodibenzofurans (TCDFs) in the vault after the fire and prior to cleanup revealed the following (highest recorded) contamination levels:(15)

Sample	PCBs	TCDFs
Soot from manhole cover	110,000 ppm	--
Wipe sample from floor	910,000 mcg/100 cm^2	--
Soot from vault wall	--	15.6 ppm

Analysis revealed 2,3,7,8-TCDD in a concentration approximately 0.1 of that detected in soot of the Binghamton State Office Building.(16)

Approximately 4,000 air samples were taken in various locations inside and outside the high-rise tower to monitor decontamination efforts. The highest air concentrations were measured in the vault; the second highest concentrations were found in the switchgear room, adjacent to the vault. Prior to cleanup, air samples in the vault revealed PCB levels up to 1,500 mcg/m^3, and air samples from the switchgear room showed PCB levels up to 98.6 mcg/m^3. The highest level outside the vault and switchgear room was found in a storage room, where a level of 12 mcg/m^3 was measured.

Chicago, Illinois

On September 28, 1983, an electrical fire in an underground PCB transformer vault forced the precautionary evacuation of a Chicago office building. The fire was caused by a 480 volt fault and resulted in the release of 15 gallons of oil from one of four transformers in the vault. The oil was composed of 65% PCBs (Aroclor 1260) and 35% trichlorobenzene. PCB contamination was limited to the vault, an adjacent fan room, underground garage, vault exhaust, sidewalk grill, and external face of the building. Analysis of the oil remaining after the fire revealed the presence of PCDFs and PCDDs. A square foot (1 ft x 1 ft) wipe sample of soot on the vault ceiling contained PCDFs and PCDDs. The results of the analysis of the oil and soot are presented in Tables 4 and 5.

Cincinnati, Ohio

On December 3, 1980, a capacitor containing PCBs for an electric motor in a unit heater overheated in a basement storage room of Our Lady of Visitation Elementary School in Cincinnati, Ohio.[18] The capacitor was used for a one-half horsepower electric motor in the unit heater. The motor's capacitor contained a design specification dielectric fluid volume of 22 ml, of which 99.6% by volume (or 21.91 ml) was a biodegradable fluid and 0.4% by volume (or 0.088 ml) was PCBs (Aroclor 1254). On March 18, 1981, the National Institute for Occupational Safety and Health (NIOSH) was requested by the Hamilton County Health Department to determine the extent of PCB contamination of the school. Air and surface wipe samples were obtained throughout the school building on March 19 and 26 to determine the presence of PCBs.

Table 4. PCBs, PCDFs, and PCDDs in the Askarel After the Chicago Fire[17]

ISOMERS	CONCENTRATION (ppb)
PCBs	650,000,000
PCDFs	
2,3,7,8-TCDF[a]	75
Total tetra-	230
Penta-	440
Hexa-	980
Hepta-	1,850
Octa-	1,600
Total PCDFs	5,100
PCDDs	
2,3,7,8-TCDD	N.D.[b] (2.5)
Total tetra-	N.D. (2.5)
Penta-	N.D. (2.5)
Hexa-	N.D. (3.0)
Hepta-	N.D. (2.0)
Octa-	8.0
Total PCDDs	8.0

[a] 2,3,7,8-TCDF and co-eluting isomers.

[b] N.D. = Not Detected; detection limits in parentheses.

Table 5. PCBs, PCDFs, and PCDDs in Wipe Samples from the Interior of the Transformer Vault from Chicago Fire[17]

ISOMERS	AMOUNT (ng/ft^2)
PCBs	20,900,000[a]
PCDFs	
2,3,7,8-TCDF[b]	3,800
Total Tetra-	28,000
Penta-	40,000
Hexa-	33,000
Hepta-	11,200
Octa-	1,238
Total PCDFs	113,438
PCDDs	
2,3,7,8-TCDD	N.D.[c] (5)
Total Tetra-	N.D. (5)
Penta-	N.D. (25)
Hexa-	N.D. (55)
Hepta-	314
Octa-	127
Total PCDDs	441

[a]PCBs from wipe of vault wall; PCDFs/PCDDs from wipe of vault ceiling.

[b]2,3,7,8-TCDF and co-eluting isomers.

[c]N.D. = Not Detected; detection limits in parentheses.

Airborne PCB concentrations were reported as micrograms (mcg) of PCBs per cubic meter (m^3) of air sampled. As seen in Table 6, PCBs were not detected in air samples obtained in the basement storage room nor in another room tested. These results were as expected, based on the extremely low vaporization rate (0.000052 $g/cm^2/hr$ at 100°C) of Aroclor 1254.

Wipe samples of surfaces were obtained by wiping an area of approximately 100 cm^2 using a Whatman smear tab moistened with pesticide quality cyclohexane. The samples were extracted using toluene and analyzed using the procedure used for the air samples. The presence of PCBs was reported as mcg per 100 cm^2 of surface area. As seen in Table 7, samples obtained from the floor, ceiling, desk, and bookshelves in the basement storage room (Room 27) showed a surface presence of < 0.05 to 7200 mcg PCBs/100 cm^2 (< 5-720,000 mcg/m^2). Background levels of PCBs on surfaces in the school showed a presence of < 0.05 to 0.45 mcg PCBs/100 cm^2 (< 5-45 mcg/m^2). Surfaces tested in buildings in eastern, central, and western Cincinnati showed a background presence of < 0.05 to 0.13 mcg/100 cm^2 (< 5-13 mcg/m^2).

The two wipe samples with the highest concentration of PCBs were also analyzed for PCDDs and PCDFs with special emphasis on the 2,3,7,8-isomers. No dibenzodioxins or dibenzofurans were detected in either of the samples. The lower limits of analytical detection using this method were 0.10 and 0.09 mcg/100 cm^2 sample, respectively.

The Health Commissioner of Hamilton County offered the following recommendations to the school:

1. The concentration of PCBs on surfaces (i.e., floor, desks, bookshelves) in Room 27 should be reduced to background levels, i.e., < 0.5 mcg PCBs/100 cm^2 surface area (50 mcg/m^2).

2. Other than Room 27, no rooms require decontamination.

The school was reopened in all areas except the wing containing the contaminated storage Room 27 and nearby classrooms 24, 25, and 26.[18]

Table 6. Analysis of PCBs in Air Samples from School in Cincinnati, Ohio[18]

SAMPLE LOCATION	VOLUME (L)	AIR SAMPLE LEVELS
Inside heating unit on floor (Room 27)	45.2	N.D.[a]
Center of room on bookshelf	43.3	N.D.
Principal's office	34.7	N.D.

[a]N.D. or Not Detected means that the PCBs were not detected at the lowest level (< 0.05 mcg/sample) capable of being measured by the analytical method equivalent to an airborne concentration of approximately < 1 mcg/m^3 for these samples.

Table 7. Summary of PCB[a] Wipe Sample Results from School in Cincinnati, Ohio[18]

SAMPLE LOCATION	NUMBER OF SAMPLES	PCBs LEVEL (mcg/100 cm^2)	
		MEAN	RANGE
Room 27 (Basement location)[b]	20	771	< 0.05-7200[c]
Room 25	4	0.08	< 0.05-0.14
Room 24	3	0.05	< 0.05-0.06[d]
Room 26	3	< 0.05	< 0.05[e]
Hallway between rooms 24-27	4	0.05	< 0.05-0.07
Room 8	4	0.06	< 0.05-0.08
Room 22	6	0.11	< 0.05-0.29
Room 9	2	0.11	< 0.05-0.16
Room 10	4	0.12	< 0.05-0.20
Room 11	2	0.09	< 0.07-0.11
Room 12	2	0.08	< 0.06-0.09
A.V. room	4	< 0.05	< 0.05
Principal's office	3	0.21	0.05-0.45
Mobile classroom	2	0.06	0.06
Background level (3 locations)	10	0.07	< 0.05-0.13

[a]Reported as Aroclor 1254.

[b]Rooms 27, 25, 26, and 24 were all in the basement.

[c]A < value means PCBs were not detected at detection limit.

[d]Excludes sample taken on capacitor surface showing PCB presence of 4.9 mcg/100 cm^2.

[e]Excludes sample taken on capacitor surface showing PCB presence of 2.3 mcg/100 cm^2.

Boston, Massachusetts

In January 1982, an electrical fire involving a transformer containing Aroclor 1254 occurred in a government office facility in Boston, Massachusetts. One bulk soot sample was spiked with 200 ng d_{12}-chrysene and was then Soxhlet-extracted for 24 hours with hot toluene. This extract was decanted and labeled fraction 1. More hot toluene was added to the sample for an additional 24 hours. The extract was labeled fraction 2. Both extracts were analyzed. 70% of the d_{12}-chrysene was recovered in fraction 1. The two extracts were concentrated. Fraction 1 required multiple HRGC-MS analysis because of its complex components. PCDFs were confirmed in fraction 1. These results are shown in Table 8.[19]

Miami, Florida

On April 13, 1982, a fire involving an electrical transformer occurred in an underground vault in Miami, Florida.[20] The International Association of Fire Fighters (I.A.F.F.) requested NIOSH to perform analyses of surface samples in order to determine if fire fighters had been exposed to PCBs or other more toxic decomposition products such as PCDDs and PCDFs.

In these analyses, NIOSH collected samples using two different methods. Wipe samples were collected using sterile cotton pads saturated with hexane from sample areas with an approximate size of 100 cm^2. Surfaces thought to be less heavily contaminated were wiped with dry Whatman smear tabs.

Table 9 presents the results of the surface sample analyses for PCB contamination. Samples taken within the vault showed the heaviest contamination. Turnout coats and other personal protective equipment were not found to be contaminated (probably due to the decision to allow the fire to self-extinguish). The only contaminated equipment at the station was found to be the smoke ejector fan. Results showed PCB contamination of > 31 mcg/100 cm^2. Previous NIOSH investigations indicate normal background levels for PCBs on non-contaminated surfaces should be less than 0.5 mcg/100 cm^2.[20]

Table 8. Levels of PCDFs and PCDDs from the Accidental Burning of PCB-Containing Electrical Equipment at Boston, Massachusetts[19]

ISOMERS	CONCENTRATION mcg/g SOOT
Total PCDFs	165
Total Tri-CDFs	50
Total Tetra-CDFs	60
2,3,7,8-Tetra-CDF	3
Total Penta-CDFs	35
Total Hexa-CDFs	15
Total Hepta-CDFs	2
Octa-CDF	N.D.[a]
Total PCDDs	N.D.
Total Tri-CDDs	N.D.
Total Tetra-CDDs	N.D.
2,3,7,8-Tetra-CDD	N.D.
Total Penta-CDDs	N.D.
Total Hexa-CDDs	N.D.
1,2,3,4,6,7,9-Hepta-CDD	N.D.
1,2,3,4,6,7,8-Hepta-CDD	N.D.
Octa-CDD	N.D.

[a]N.D. = Not Detected; detection limit at 100 ng/g = 0.1 mcg/g = 0.1 ppm.

Table 9. PCB Residue from a Transformer Vault Fire, Collected 4/16/82 in Miami, Florida[20]

SAMPLE LOCATION/DESCRIPTION	SAMPLE TYPE	PCBs[a] (mcg/100 cm^2)
Inside Transformer Vault:		
Wall behind removed transformer (soot)	wipe	434[b]
Top of primary cable above fire (soot)	wipe	389
Primary cable support bracket (soot)	wipe	704
Floor near base of isolating switch (dirt)	wipe	27,400
Ceiling near fire location (soot)	wipe	860
Secondary bus near vault ceiling (dirt)	wipe	195
Wall next to exit ladder (dust)	smear tab	2
Rung of exit ladder (dust)	smear tab	79
Above Transformer Vault:		
Sidewalk grating	smear tab	2
Standing water at curb near vault	wipe	3
Fire Fighters' Clothing and Equipment:		
Sleeves of turnout coat	smear tab	< 0.1
Top of boot	smear tab	< 0.1
Inside helmet	smear tab	< 0.1
Front of turnout coat	smear tab	< 0.1
Inside helmet face shield	smear tab	< 0.1
Outside facepiece	smear tab	< 0.2
Smoke ejector fan	smear tab	> 31

[a]As Aroclor 1260 (used as standard for quantitation of samples).

[b]As mixture of Aroclor 1254 (231 mcg) and Aroclor 1260 (203 mcg).

Table 10 presents the results of the analyses of 6 bulk samples of soot and other fire residues for the presence of PCDD and PCDF isomers. No PCDDs were detected in these samples, but PCDFs from trichloro- to hexachloro-isomers were detected in samples B1 to B6. The samples also exhibited high levels of PCBs through Cl_{10} and polychlorinated diphenylethers (PCDEs) through Cl_8. The highly toxic 2,3,7,8-tetrachloro isomer was not detected in any of these samples.

Gas chromatograph/mass spectrometer (GC/MS) analyses of soot samples collected from the vault ceiling directly above the fire scene were also performed. Peaks identified included penta-, hexa-, and heptachlorobiphenyls, and numerous alkanes, mostly larger than C_{20}.[20]

Table 10. Results of Analyses of PCDDs and PCDFs in Bulk Samples of Residue from Miami Transformer Fire[20]

ISOMERS	NUMBER POSSIBLE	NUMBER DETECTED						CONCENTRATION IN SAMPLE (ng/g or ppb)					
Samples:		B1[a]	B2	B3	B4	B5	B6	B1	B2	B3	B4	B5	B6
Mono-CDD[b]	2	0	0	0	0	0	0	N.D.[c]	N.D.	N.D.	N.D.	N.D.	N.D.
Di-CDD	10	0	0	0	0	0	0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Tri-CDD	14	0	0	0	0	0	0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Tetra-CDD	22	0	0	0	0	0	0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Penta-CDD	14	0	0	0	0	0	0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Hexa-CDD	10	0	0	0	0	0	0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Hepta-CDD	2	0	0	0	0	0	0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Octa-CDD	1	0	0	0	0	0	0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
2,3,7,8-TCDD	1	0	0	0	0	0	0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

[a]Sample Description/Location:
- B1 Soot, dust, and dirt from top of primary cable support bracket, circuit #2.
- B2 Residue from floor under isolating switch near burned transformer.
- B3 Scrapings from ceiling above transformer.
- B4 Scrapings from secondary bus.
- B5 Vault wall near exit ladder.
- B6 Scrapings of soot and dirt from smoke ejector fan used to exhaust smoke from vault during fire.

[b]Detection Limit for PCDDs = 10 ng/g for samples B1, B5, and B6; 100 ng/g for samples B2, B3, and B4.

[c]N.D. = Not Detected.

Table 10. Results of Analyses of PCDDs and PCDFs in Bulk Samples of Residue from Miami Transformer Fire (Continued)

ISOMERS	NUMBER POSSIBLE	NUMBER DETECTED						CONCENTRATION IN SAMPLE (ng/g or ppb)					
Samples:		B1[a]	B2	B3	B4	B5	B6	B1	B2	B3	B4	B5	B6
Mono-CDF[b]	4	0	0	0	0	0	0	N.D.[c]	N.D.	N.D.	N.D.	N.D.	N.D.
Di-CDF	16	0	0	0	0	0	0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Tri-CDF	28	6	0	0	0	0	6	180	N.D.	N.D.	N.D.	N.D.	110
Tetra-CDF	38	6	0	0	0	0	7	530	N.D.	N.D.	N.D.	N.D.	280
Penta-CDF	28	7	0	0	0	0	5	1000	N.D.	N.D.	N.D.	N.D.	290
Hexa-CDF	16	3	0	0	0	0	4	180	N.D.	N.D.	N.D.	N.D.	100
Hepta-CDF	4	0	0	0	0	0	0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Octa-CDF	1	0	0	0	0	0	0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
2,3,7,8-TCDF	1	0	0	0	0	0	0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

[a]Sample Description/Location:
- B1 Soot, dust, and dirt from top of primary cable support bracket, circuit #2.
- B2 Residue from floor under isolating switch near burned transformer.
- B3 Scrapings from ceiling above transformer.
- B4 Scrapings from secondary bus.
- B5 Vault wall near exit ladder.
- B6 Scrapings of soot and dirt from smoke ejector fan used to exhaust smoke from vault during fire.

[b]Detection Limit for PCDFs = 10 ng/g for samples B1, B2, B5, and B6; 50 ng/g for sample B4; 100 ng/g for sample B3.

[c]N.D. = Not Detected.

Columbus, Ohio

In March 1984, a capacitor fire occurred in a Columbus office building. The capacitor was filled with Aroclor 1242. Analysis of soot samples revealed the presence of PCDFs and trace amounts of PCDDs (tetra- to octa-isomers). Chlorobenzene was also detected in trace amounts with a detection limit at ppm level. Analysis of wipe samples indicated the presence of PCDFs and PCDDs.[21,22] Table 11 presents the results of the analyses of the soot and wipe samples.

Table 11. Analysis of Wipe and Soot Samples from Columbus Fire[21,22]

SAMPLE	ISOMER	TOTAL CONCENTRATION
Wipe	2,3,7,8-TCDF	≤ 1,000 ng
	Total PCDFs	≤ 10,000 ng
	2,3,7,8-TCDD	≤ 3.0 ng
	Total PCDDs	≤ 44 ng
Soot	Total PCDFs	10.9 ppm
	Total PCDDs (tetra to octa)	Trace[a]
	Chlorobenzene	Trace[a]

[a]Detection limit at ppm level.

St. Paul, Minnesota

On June 22, 1982, a PCBs fire occurred at the Hill-Murray High School in St. Paul, Minnesota.[23] NIOSH samples of surface wipes and air were obtained on June 23, 1982, and again on July 7. The results of the analyses are reported in Tables 12 and 13.

Norrtalje, Sweden

On September 25, 1978, there was an intense fire in a capacitor battery north of Norrtalje, Sweden. The fire could not be extinguished for over 30 minutes while high voltages were turned off. Eighteen PCBs-containing

Table 12. Analysis of PCBs (Reported as Aroclor 1260) in Wipe Samples from the Hill-Murray School[23]

	PCBs (mcg/100 cm^2)	
SAMPLE LOCATION	**6/23/82**	**7/7/82**
Vault Room	100-5000	2-120
Vault Door	< 5	
Corridor outside Vault Room	< 5	
Room 048	20	3
Boiler Room	< 5	
Cafeteria	0.22-0.24	< 0.05
Corridor leading to the Fieldhouse	< 0.05	< 0.05
Corridor wall across from Room 109	0.26	< 0.05
Corridor wall adjacent to Music Suite	0.27	
Corridor wall leading to Office	1.6	< 0.05
Outside Room 106	5.8	
Room 106	0.61-0.95	0.8
Room 138	1.4-2.1	0.2-0.5
Gymnasium	0.29	
Athletic Building lobby	0.14	
Priory	< 0.05	

Table 13. Area Concentrations of PCBs (Reported as Arcolor 1260) and Chlorinated Benzenes at Hill-Murray School[23]

SAMPLE VICINITY BY DATE	SAMPLE DURATION (HOURS)	SAMPLE VOLUME (LITERS)	AIRBORNE CONCENTRATION (mg/m^3) PCBs[a]	TOTAL TRICHLORO-BENZENE[b]	TOTAL TETRACHLORO-BENZENE[c]
June 23, 1982					
Transformer Vault	2.54	137	0.05	22.6	18.2
Transformer Vault	2.52	136	0.09	17.6	25.7
Vault Doors	2.37	123	0.02	10.2	11.7
Room 018	3.06	165	0.004	0.73	1.21
Outside Room 109	2.67	144	< 0.001	0.12	0.26
Cafeteria	2.98	161	< 0.001	0.35	0.27
July 7, 1982					
Transformer Vault	2.82	169	0.007	0.331	0.651
Vault Doors	2.83	170	< 0.001	0.048	0.229
Outside Room 018	2.82	169	< 0.001	0.020	0.089
Outside Room 109	2.92	175	< 0.001	0.011	0.037
Cafeteria	2.92	175	< 0.001	0.010	0.032

[a]NIOSH recommended permissible exposure limit for an 8-hour time-weighted average (TWA) exposure criteria is 0.001 mg/m^3.

[b]ACGIH threshold limit value is 40 mg/m^3 for 8-hour TWA. Neither NIOSH nor OSHA have exposure criteria.

[c]No 8-hour TWA exposure criteria.

capacitors (100 kVA each) were involved in the fire. When the capacitors were demounted, some showed no signs of damage while others had exploded, releasing their contents. B. Jansson and G. Sundstrom, at the Special Analytical Laboratory, National Swedish Environmental Protection Board located at the University of Stockholm, were contacted a few weeks after the accident and asked to perform sample analysis for PCDF formation.[24] Up to 300 mg samples together with 100 ng [2,3,7,8-^{37}Cl]-tetrachloro-[1,4,6,9-^{2}H]- dibenzo-p-dioxin as the internal standard dissolved in 1 ml n-hexane were chromatographed on aluminum oxide. The first fraction containing most of the PCBs was eluted with 90 ml 5% dichloromethane in n-hexane. The second fraction, which was eluted with 60 ml dichloromethane, contained all PCDF references, the internal standard, and at least two PCBs.

Results of the analyses are given in Table 14. An Aroclor 1242 standard was used as a reference. Samples were taken from intact and exploded capacitors, from the wire fence surrounding the capacitors (fence was washed with acetone to obtain sample), and from pine tree needles which were located about 10 meters (m) downwind from the fire.

The wire fence was found to contain unexpectedly low PCB concentrations. The extractable part contained only 0.3 mg PCBs per g extractables. As a result of this low PCB level, the upper limit of the PCDF/PCB ratio for the fence extract becomes high. While no presence of PCDF was found in the fence sample, if the extremely high detection limit for the dichlorinated compounds is excluded, the highest possible concentration should be about 300 mcg per g PCBs.

In addition to these environmental samples, blood samples were taken from six firemen who were exposed to the fire. The samples were not taken until a few weeks after the fire incident. At that time the PCB levels in the blood samples were within the same range (2.3 to 3.6 mg PCBs/g) as those for unexposed Swedes.[24]

Table 14. PCB and PCDF Levels in Capacitors and Environmental Samples at Norrtalje, Sweden[9,24]

SAMPLE	PCBs[a] (g/g)	PCDF SAMPLE (mcg/g)					PCDF/PCB (mcg)
		MONO-CDF	DI-CDF	TRI-CDF	TETRA-CDF	PCDF	
Liquid in intact capacitor	0.83-0.86	0.2-0.5	0.2	0.2-0.3	0.2-0.3	0.9-1.1	1.1-1.3
Liquid in exploded capacitor	0.93	24	38	11	3	75	81
Liquid on exploded capacitor	0.49-0.60	12-21	9-21	3-7	2	27-52	45-107
Extract from wire fence	0.3×10^{-3}	< 0.03	< 0.2	< 0.03	< 0.04	< 0.3	--
Pine needles	0.3×10^{-6}	N.D.[b]	N.D.	N.D.	N.D.	N.D.	--

[a]Aroclor 1242.

[b]N.D. = Not Detected.

Stockholm, Sweden

On August 25, 1981, an explosion (electrical arc) took place in an 11 kV capacitor battery in an electrical power station in Stockholm, Sweden. The explosion was caused by an electrical failure in the capacitor battery that was so violent that it caused the wall to rupture. Wipe samples were taken about 1 m from the capacitor and were tested for PCDF and PCDD levels. Extraction and measurement were accomplished by spiking the wipe tests with 1-5 ng of labeled CDD. The sample was treated with 10 ml of 1M HCl for 1 hour. The slurry was filtered and dried, extracted with toluene, and dried with N_2. The residues were redissolved in 2 ml of n-hexane, added to a silica gel column and eluted with 5 ml of n-hexane. The hexane was evaporated with N_2 until 10 mcl remained. PCDDs and PCDFs were separated from other polychlorinated impurities using an Alox-column. The first fraction, 10 ml n-hexane:methylene chloride (98:2), was discharged. The second fraction, 10 ml n-hexane:methylene chloride (1:1), was collected and dried in N_2. This residue was used in the GC/MS analyses. Individual MS-response factors were used to calculate levels given in Table 15. The total levels of polychlorinated biphenylenes (PCBPs) were reported to be 25-30 mcg/m^2.[9,13,25] Polychlorinated pyrenes (PCPYs) were also detected but not quantified.

Skövde, Sweden

On March 19, 1982, a violent fire broke out in a capacitor battery (400 V) serving a high-frequency oven in a metal treatment factory in Skövde, Sweden. The dielectric fluid in the capacitors consisted of either mineral oil or PCBs, and both types of capacitors were in use. There were no chlorinated benzene additives in the oil. The fire started in a mineral oil capacitor and 2 hours elapsed until the fire was extinguished. The smoke spread to an extent of 1800 m^2 (60 m x 30 m). Copper bars for electricity in the capacitor room ceiling partially melted (m.p. 1080°C). The capacitor battery contained 21 capacitors filled with PCBs (5 kg each). After the fire, 12 of these capacitors had been opened and 9 remained sealed.

Wipe tests (tissue 1 dm^2) were used to take samples from a) the floor of the capacitor battery, b) the floor close to the battery, c) the wall of the

Table 15. Concentrations of PCDFs Found in Samples from an Accidental PCB Fire in Stockholm, Sweden[9,13,25]

PCDF	PCDF CONCENTRATION (ng/m^2)
2,3,7,8-Tetra-CDF	150
1,2,7,8-Tetra-CDF	150
2,3,6,8-Tetra-CDF	125
1,4,6,9-Tetra-CDF	75
2,4,6,7-Tetra-CDF	37
3,4,5,7-Tetra-CDF	7.5
1,3,6,7- and 1,3,6,9-Tetra-CDF	300
Other Tetra-CDFs	750
Total Tetra-CDFs	1200
2,3,4,7,8-Penta-CDF	45
1,2,4,7,8-Penta-CDF	38
1,2,3,6,7-Penta-CDF	15
1,3,4,7,8-Penta-CDF	11
2,3,4,6,7-Penta-CDF	7.5
1,2,4,6,8-Penta-CDF	3.8
1,2,4,7,8-Penta-CDF	3.8
1,2,3,6,7-Penta-CDF	3.8
1,2,4,8,9-Penta-CDF	3.8
2,3,4,6,8-Penta-CDF	2
1,2,3,7,8- and 1,2,3,4,8-Penta-CDF	15
Other Penta-CDFs	19
Total Penta-CDFs	175
Total Hexa-CDFs	< 0.5

capacitor room, 2 m from the battery, 3 m above the floor, and d) the bench 10 m from the oven (1 floor above the capacitor). Table 16 shows the results of the analysis. High levels of PCDFs (> 0.10 mcg/g) could only be found close to the fire. Although polychlorinated pyrenes were detected, no PCDDs or PCBPs could be identified in the samples from this fire.(9,13,25)

Table 16. Levels of PCDFs in Wipe Samples from the Skövde Fire(9,13,25)

ISOMER	CONCENTRATION (ng/m^2) SAMPLE NUMBER			
	1	2	3	4
2,3,7,8-Tetra-CDF	20	100	< 1	< 1
Total Tetra-CDFs	100	600	< 1	10[a]
Total Penta-CDFs	40	100	< 1	< 1
Total Hexa-CDFs	40	60	< 1	< 1
Total Hepta-CDFs	8	8	< 1	< 1
Octa-CDF	5	5	< 1	< 1

[a]Different isomers than found in samples 1 and 2.

Surahammar, Sweden

On September 23, 1982, a 500-unit capacitor battery at a steel mill in Surahammar, Sweden, was ignited by 5 tons of molten steel (1500°C). The capacitors were filled with PCBs (2 tons) and mineral oil (3 tons). A violent fire broke out and burned for 2 to 3 hours filling the entire building (140 m x 70 m x 25 m) with smoke.(9) Table 17 presents the results of analyses of the wipe samples.

Imatra, Finland

On August 3, 1982, a bank of capacitors in a paper mill outside Imatra was destroyed by explosions and fire. The fire was localized in the capacitor bank behind the 10 kV contactor station. Soot and gas had spread with the pressure wave through an open doorway to the 10 kV contactor station and the adjacent 3 kV contactor station, and through cable holes to the storage space directly above the contactor stations, to the floor beneath, and to the instrument cross-connection room.

Table 17. PCDFs Found in Wipe Tests at Surahammar, Sweden (ng/m^2)[9]

SAMPLE LOCATION	TOTAL TCDFs	2,3,7,8-TCDF	Cl_5	Cl_6	Cl_7	Cl_8
Capacitor Room (Sample 1)	4000	875	3300	1800	1500	300
Capacitor Room (Sample 2)	1100	365	1250	940	625	145
N.E. Corner, 10 m height	1250	300	355	150	65	13
S.E. Corner, 10 m height	480	120	210	140	60	30
N.E. Corner, floor	100	25	27	15	5	2
S.E. Corner, floor	90	22	25	17	17	4
10 m Outside, downwind	< 250	< 25	< 25	< 60	58[a]	17[a]
300 m Outside, downwind	< 250	< 25	< 25	< 60	< 30	< 12
After Cleaning (Sample 1)	< 20	< 4	< 10	< 12	< 15	2[a]
After Cleaning (Sample 2)	< 40	< 8	< 20	< 20	< 30	6[a]

[a]Possibly due to use of decachlorophenyl as an additive in casting wax.

Each capacitor contained 20 liters of Clophen A 30 (a mixture of PCBs with an average chlorine content of 42%). Soot samples were analyzed for PCDFs and PCDDs. The results are included in Table 18.

Table 18. Levels of PCDFs and PCDDs in Soot Samples from Imatra, Finland Fire[9,10]

ISOMERS	CONCENTRATION (ppm)		
	SAMPLE 1	SAMPLE 2	SAMPLE 3
PCDFs			
Mono-CDFs	80	--	--
Di-CDFs	250	--	--
Tri-CDFs	200	--	--
Tetra-CDFs	20	16	1.0
2,3,7,8-Tetra-CDF	--	1.0	0.07
Penta-CDFs	1	1.0	0.2
Hexa-CDFs	--	0.3	0.04
Hepta-CDFs	--	0.2	0.02
Octa-CDF	--	0.1	0.01
PCDDs	N.D.[a]		

[a]N.D. = Not Detected.

Hallstahammar, Sweden

On November 8, 1982, a capacitor exploded in a foundry in Bulten-Kanthal in Hallstahammar, Sweden. The capacitor was located close to a melting oven in the ground floor, and the fumes spread through the entire building (40 m x 15 m x 5 m). Wipe tests were collected for analysis and the results are presented in Table 19.

Table 19. Levels of PCDFs in Wipe Samples from Hallstahammar, Sweden Fire[9]

SAMPLE	CONCENTRATION (ng/m^2)					
	TOTAL TCDFs	2,3,7,8-TCDF	PeCDFs	HxCDFs	HpCDFs	OCDF
Copper bar, 2 dm above	1600	540	360	600	800	1340
Bar, 5 m above	5000	1000	1800	850	550	440
Floor	50	10	12	10	30	20

Railway Locomotive, Sweden

During the winter of 1982/83 a capacitor exploded in a railway locomotive in southern Sweden. The incident was not reported immediately and therefore, the samples were not collected until February 1983. The results of the analysis are given in Table 20.

Table 20. Levels of PCDFs in Railway Locomotive in Sweden[9]

SAMPLE	CONCENTRATION (ng/m^2)					
	TOTAL TCDFs	2,3,7,8-TCDF	PeCDFs	HxCDFs	HpCDFs	OCDF
Floor below capacitor	69,000	1,700	29,000	14,000	6,200	1,400
1 m from capacitor	4,900	120	1,500	400	170	40

Kisa, Sweden

On April 25, 1983, a PCB-filled capacitor exploded at the debarking line in a saw mill in Kisa, Sweden. The explosion was associated with external arcing and fuming, causing the dielectric fluid to be sprayed around. Three days following the explosion, samples were taken for analysis. The results are presented in Table 21.

Table 21. Levels of PCDFs in Wipe Samples from Kisa, Sweden Explosion[9]

SAMPLE	CONCENTRATION (ng/m^2)					
	TOTAL TCDFs	2,3,7,8-TCDF	PeCDFs	HxCDFs	HpCDFs	OCDF
Near capacitor	100,000	40,000	N.A.[a]	N.A.	N.A.	N.A.
Closed operator room	500	125	N.A.	N.A.	N.A.	N.A.
Near capacitor after cleaning	< 90	< 21	70	30	< 10	5
Closed operator room after cleaning	< 12	< 5	< 5	< 5	< 5	5

[a]N.A. = Not Analyzed.

Reims, France

On January 14, 1985, a violent transformer explosion occurred in a 6-story building in Reims, France. The transformer was filled with an askarel of 60% PCBs and 40% tetrachlorobenzene. The dirty, highly contaminated soot was analyzed on February 21, 1985 and April 2, 1985. The results of these analyses are presented in Table 22.

Other Fires

There have been a host of other fires associated with PCB transformers and capacitors. Many in the U.S. probably go unreported. Table 23 lists some other fire incidents that have been reported.

Table 22. Levels of PCDFs and PCDDs in Soot Samples from Reims, France Explosion [26]

ISOMER	CONCENTRATION (mcg/m^2)					
	SAMPLE NUMBER					
	1	2	3	4	5	6
Tetra-CDFs	>30	>8	>4.5	0.11	0.22	0.38
Penta-CDFs	960	590	37	0.89	1.5	1.40
Hexa-CDFs	760	570	36	0.70	1.2	1.90
Hepta-CDFs	530	490	27	1.2	1.9	3.3
Octa-CDF	290	220	36	N.A.[a]	N.A.	N.A.
Tetra-CDDs	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
Penta-CDDs	<1	<1	<0.005	<0.005	<0.005	<0.005
Hexa-CDDs	<1	<1	<0.005	<0.005	<0.005	<0.005
Hepta-CDDs	35	32	<0.005	0.11	0.14	0.33
Octa-CDD	16	14	<0.005	0.18	3.45	0.33

[a]N.A. = Not analyzed

Samples 1 and 2 were taken on the ceiling of the basement near the door of the transformer vault (February 21).
Sample 3: wipe sample collected externally on the door of the transformer vault (February 21).
Sample 4: wipe sample on the second floor, near the door of an apartment (April 2).
Sample 5: wipe sample in a bathroom, second floor (April 2).
Sample 6: wipe sample in a kitchen, second floor (April 2).
Samples 4,5, and 6 were collected after cleaning.

Table 23. PCDF Levels in Other PCB Fires[27]

SITE	PCDF LEVELS	PCBP LEVELS
Danviken, Sweden	1.5 mcg/m^2	None
Helsinki, Finland	--	--
Halmstad, Sweden	--	--
Arvika, Sweden	--	--
Kaukopää, Sweden	None	None

CONTAMINATION CLEANUP CRITERIA

There are no Federal guidelines to define acceptable cleanup levels for toxic releases from PCB transformer and capacitor fires. Current regulations state, however, that all spills and leaks of PCBs or dioxins-contaminated material should be cleaned up to preexisting background levels whenever there is a threat of contamination of water, food, feed, or humans. NIOSH has detected background levels in urban areas of up to 0.5 mcg PCBs/100 cm^2 of surface area. Following the occurrence of PCBs-related fire incidents, several states and other countries have established contamination cleanup criteria. These criteria are presented in Table 24.

Table 24. Contamination Cleanup Criteria[10,13,15,27]

LOCATION	CONTAMINANT	AIR	SURFACE
Binghamton, NY Building	PCDDs/PCDFs	10 pg/m^3 of 2,3,7,8-TCDD/TCDF	3 pg/m^2 of 2,3,7,8-TCDD/TCDF
	PCBs	200 ng/m^3 of PCBs	60 mcg/m^2 of PCBs
Inside Vault	PCDDs/PCDFs	80 pg/m^3 of 2,3,7,8-TCDD/TCDF	24 ng/m^2 of 2,3,7,8-TCDD/TCDF
	PCBs	1 mcg/m^3 of PCBs	1 mg/m^2 of PCBs
San Francisco, CA	PCDDs/PCDFs	10 pg/m^3 of 2,3,7,8-TCDD/TCDF	3 pg/m^2[a]
	PCBs	200 ng/m^3 of PCBs	60 mcg/m^2 of PCBs
Inside Vault	PCDDs/PCDFs	80 pg/m^3 of 2,3,7,8-TCDD/TCDF	24 ng/m^2 of 2,3,7,8-TCDD/TCDF
	PCBs	1 mcg/m^3 of PCBs	1 mg/m^2 of PCBs

[a]Sum of all PCDD/PCDF isomers Cl_4 - Cl_7 with Cl substitution in the 2,3,7, and 8 positions.

Table 24. Contamination Cleanup Criteria (Continued)

LOCATION	CONTAMINANT	AIR	SURFACE
Sante Fe, NM	PCDDs/PCDFs	---	1 ng/m^2 of 2,3,7,8-TCDD/TCDF
Finland	PCDDs/PCDFs	---	5 ng/m^2 of 2,3,7,8-TCDD/TCDF
Sweden	PCDDs/PCDFs	---	50 ng/m^2 of total TCDF

SECTION 4

PCDFs, PCDDs, AND PCBPs FROM THE PYROLYSIS OF PCB FLUIDS

The formation of PCDFs and PCDDs has been attributed to the range of chemical reactions that occur during the pyrolysis of PCBs, the condensation of chlorobenzenes, and the condensation or dimerization of chlorophenols. PCBs and chlorobenzenes are major components of most PCB transformer fluids, whereas the chlorophenols are intermediates formed in the range of 550 to 700°C. The amounts of these compounds formed during the combustion process vary with temperature and concentration.

FORMATION OF PCDFs FROM PCBs

Laboratory studies have indicated that with adequate reaction time and efficient mixing between air and fuel, PCBs are completely decomposed into H_2O, CO_2, and HCl at a temperature range of 800-1000°C. Pyrolytic conditions, however, allow the formation of PCDFs. The pyrolysis of commercial PCBs yields about 30 major, and more than 30 minor, PCDFs and an indeterminable number of PCBPs.

The importance of combustion as a source of PCDDs and PCDFs (and various chlorohydrocarbons) was discovered in 1977, when these toxic materials were found in fly ash and flue gases of municipal incinerators.

In 1978, Morita reported that heating Aroclor 1248 to 300°C in a sealed glass ampoule for 2 weeks produced approximately a 4-fold increase in the amount of PCDFs.[28] In the presence of oxygen, PCDFs formation began when samples were heated for 1 week above 270°C, reaching a maximum of approximately 0.2% conversion at 300°C. Dichloro- and trichlorodibenzofurans were also formed from the tetrachlorobiphenyls in Aroclor 1248.

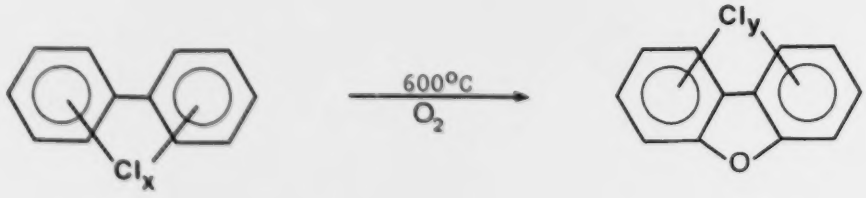
In a study by Buser *et al.*, Aroclor 1254 was pyrolyzed at temperatures of 550°-750°C in quartz mini-ampoules.[29] GC/MS analysis showed PCDFs were formed in the process. The results are presented in Table 25.

Table 25. Pyrolysis of Aroclor 1254 in Quartz Mini-Ampoules[29]

TEMP. (°C)	AMT. (mcg)	DECOMP. (%)	PCDFs FORMED[a] (%)					
			MONO-	DI-	TRI-	TETRA-	PENTA-	TOTAL
550	100	12	0.25	0.65	0.90	0.75	0.20	2.75
"	10	80	0.02	0.40	0.70	0.70	0.15	1.97
600	100	45	0.10	0.40	0.70	0.60	0.12	1.92
"	10	90	<0.01	0.10	0.25	0.35	0.05	<0.76
650	100	90	<0.01	0.02	0.18	0.25	0.12	<0.58
"	10	98	0.01	0.12	0.25	0.12	<0.02	<0.52
700	100	>99.9	<0.01	<0.01	<0.01	<0.02	<0.02	<0.07
"	10	>99.9	<0.01	<0.01	<0.01	<0.02	<0.02	<0.07
750	100	>99.9	<0.01	<0.01	<0.01	<0.02	<0.02	<0.07

[a]Combined values of all isomers of a PCDF.

Mono- to penta-CDFs were found at temperatures of 550°-650°C at levels ranging from < 0.01-0.90%. The maximum amounts were found at 550°C. Considering the amount of PCBs recovered after pyrolysis, the total yield of PCDFs ranged from 3-25%.



PCBs

x = 1 to 8
> 30 isomers

PCDFs

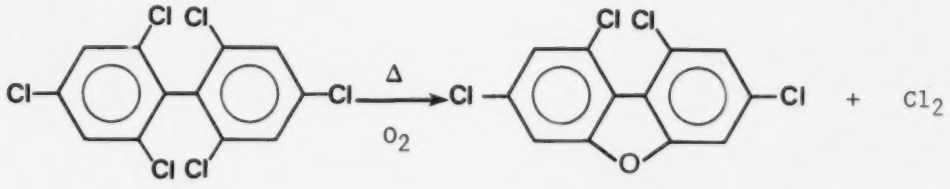
y = 1 to 6 (yield 3-25%)
> 60 isomers

Buser and Rappe, in subsequent studies, pyrolyzed 18 individual PCB isomers in the presence of air at 600°C in sealed ampoules.[29,30,31] It was found that the cyclization process which yields PCDFs from PCBs was intermolecular and followed several competing reaction pathways.[30,31] In addition to PCDFs, polychlorinated biphenylols identified as possible precursors, were present at levels of approximately one-fifth of the amount of PCDFs present.

From this work, four thermochemical reaction mechanisms were proposed for formation of PCDFs from PCBs.

1. Mechanism 1: Loss of *Ortho*-Cl_2

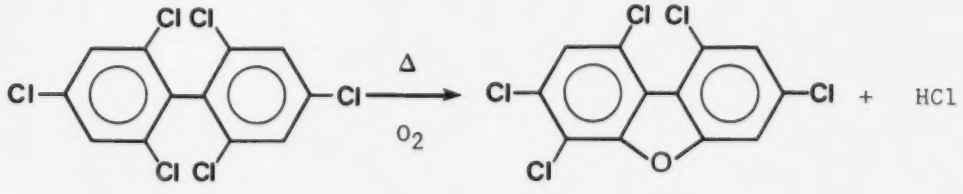
Example:



2,4,6,2',4',6'-Hexachlorobiphenyl 1,3,7,9-Tetrachlorodibenzofuran

2. Mechanism 2: Loss of HCl Involving 2,3-Chlorine Shift at the Benzene Nucleus

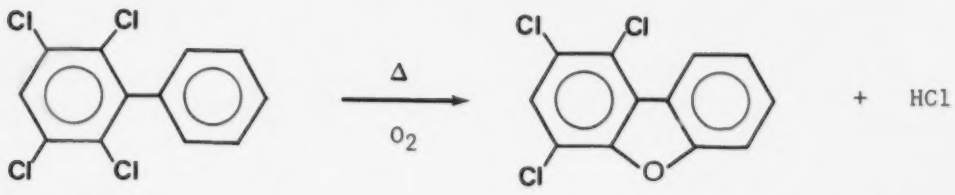
Example:



2,4,6,2',4',6'-Hexachlorobiphenyl 1,3,4,7,9-Pentachlorodibenzofuran

3. Mechanism 3: Loss of *Ortho*-HCl

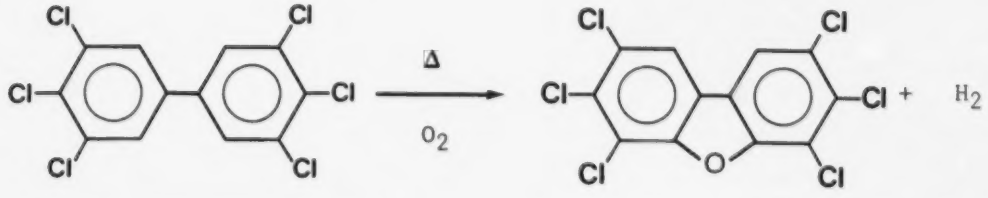
Example:



2,3,5,6-Tetrachlorobiphenyl 1,2,4-Trichlorodibenzofuran

4. Mechanism 4: Loss of *Ortho*-H_2

Example:



3,4,5,3',4',5'-Hexachlorobiphenyl 2,3,4,6,7,8-Hexachlorodibenzofuran

Table 26 summarizes the results observed by Buser and Rappe, including each chlorinated biphenyl isomer, its chlorinated dibenzofuran reaction products, and the associated thermochemical reaction mechanism.

EPA, through a contract with Midwest Research Institute, Kansas City, MO, has recently conducted several studies to evaluate thermal degradation products from dielectric fluid using a bench scale thermal destruction system.[7] The purpose of this study was to optimize conditions for PCDF formation in order to examine the potential for formation of PCDFs and PCDDs from combustion of selected PCB-containing dielectric fluids. The first part

Table 26. Thermochemical Conversion of PCBs to PCDFs[30,31]

PCB CONGENER	PCDF REACTION PRODUCTS	REACTION MECHANISM
2,3,4,5-Tetrachlorobiphenyl	1,2,3,4-TCDF[a]	4
	2,3,4-TriCDF[a,b]	3
2,3,5,6-Tetrachlorobiphenyl	1,2,4-TriCDF[a]	3
2,6,2',6'-Tetrachlorobiphenyl	1,4,9-TriCDF[a,b]	2
	1,9-DiCDF[a]	1
2,3,4,5,6-Pentachlorobiphenyl	1,2,3,4-TCDF[a]	3
2,4,5,2',5'-Pentachlorobiphenyl	2,3,8-TriCDF[b]	1
2,4,5,2',5'-Pentachlorobiphenyl	2,3,6,8- and 2,3,4,8-TCDF[a]	2
2,4,5,2',5'-Pentachlorobiphenyl	2,3,6,9-[a] and 1,3,4,8-TCDF[a]	3
2,4,5,2',5'-Pentachlorobiphenyl	1,3,4,6,9-PeCDF[a]	4
2,4,5,3',4'-Pentachlorobiphenyl	2,3,7,8-[b] and 2,3,6,7-TCDF[a]	3
2,4,5,3',4'-Pentachlorobiphenyl	1,3,4,7,8- and 1,3,4,6,7-PeCDF[a]	4
2,4,6,2',4'-Pentachlorobiphenyl	1,3,7-TriCDF[b]	1
2,4,6,2',4'-Pentachlorobiphenyl	1,3,6,7- and 1,3,4,7-TCDF[a]	2
2,4,6,2',4'-Pentachlorobiphenyl	1,3,7,9-TCDF	3
2,3,6,2',5'-Pentachlorobiphenyl	1,4,8-[a,b] and 1,2,8-TriCDF[a,b]	1
	1,4,6,8-[a,b], 1,2,6,8-[a], and 1,2,4,8-TCDF[a]	2
	1,2,6,9-[a] and 1,4,6,9-TCDF[a]	3
2,3,6,2',4',6'-Hexachlorobiphenyl	1,4,6,9-[a], 1,2,6,9-[a], and 1,2,8,9-TCDF[a]	1
	1,2,4,8,9-[b] and 1,2,4,6,9-PeCDF[a,b]	2
3,4,5,3',4',5'-Hexachlorobiphenyl	2,3,4,6,7,8-HxCDF	4
2,4,5,2',4',5'-Hexachlorobiphenyl	2,3,7,8-TCDF[b]	1
	2,3,4,7,8-TCDF	2
	1,3,4,7,8-TCDF	3
2,4,6,2',4',6'-Hexachlorobiphenyl	1,3,7,9-TCDF	1
	1,3,4,7,9-PeCDF	2

[a]Tentative isomer identification.

[b]Major isomer among reaction products.

Table 26. Thermochemical Conversion of PCBs to PCDFs (Continued)

PCB CONGENER	PCDF REACTION PRODUCTS	REACTION MECHANISM
2,4,5,2',4',6'-Hexachloro-biphenyl	1,3,7,8-TCDF[a,b]	1
	2,3,4,7,9-[a] and 1,3,4,7,8-PeCDF	2
	1,3,4,7,9-PeCDF	3
2,3,4,2',3',4'-Hexachloro-biphenyl	3,4,6,7-TCDF	1
	1,2,3,6,7-PeCDF	3
2,3,5,2',3',5-Hexachloro-biphenyl	2,4,6,8-TCDF	1
	1,2,4,6,8-PeCDF	3
2,3,4,5,2',3',4'-Heptachloro-biphenyl	2,3,4,6,7-PeCDF	1
	1,2,3,4,6,7-[a] and 1,2,3,6,7,8-HxCDF[b]	3
	1,2,3,4,7,8,9-HpCDF[a]	4
	1,2,3,4,6,7,8- and 1,2,3,4,6,7,9-HpCDF[a]	?
2,3,4,5,2',4',5'-Heptachloro-biphenyl	2,3,4,7,8-PeCDF[b]	1
	2,3,4,6,7,8-HxCDF	2
	1,2,3,4,7,8- and 1,3,4,6,7,8-HxCDF[a,b]	3
	1,2,3,4,6,7,9-HpCDF[a]	4
2,3,4,5,2',3',4',5'-Octa-chlorobiphenyl	2,3,4,6,7,8- and other HxCDFs	1
	1,2,3,4,6,7,8-HpCDF[b]	3
	OCDF	4

[a]Tentative isomer identification.

[b]Major isomer among reaction products.

of the experiment was designed to determine the optimum temperature, oxygen, and residence time conditions for PCDF formation. The feed into the system was mineral oil spiked with three individual PCB congeners (2,3,4,6-tetrachlorobiphenyl; 3,4,5,3',4',5'-hexachlorobiphenyl; and 2,4,6,2',4',6'-hexachlorobiphenyl), which form PCDFs by the four reaction mechanisms proposed by Buser and Rappe.[29,30,31] Statistical analysis of the results of 33 runs indicates that both temperature and oxygen have significant effects on the PCDF yield and that the interaction between temperature and oxygen is synergistic. The results indicate that the optimum conditions for PCDF formation from PCBs are a temperature of 675°C for ≥ 0.8 second, with an excess oxygen concentration of 8%. The residence time, in the range of 0.3 to 1.5 seconds, did not significantly affect the yield, although the observed yields of PCDFs were lower at shorter residence times.

In the next part of the study, duplicate test runs were conducted with mineral oil and silicone oil dielectric fluids containing PCBs (Aroclor 1254) at concentrations of 0, 5, 50, and 500 ppm. An askarel fluid containing 70% Aroclor 1254/30% trichlorobenzenes, and a non-PCB askarel fluid containing mostly trichlorobenzenes with some tetrachlorobenzenes, were tested in duplicate. PCDFs were found in all samples. PCDDs were found in the samples from the trichlorobenzene runs and occasionally at low levels in some of the other samples. Up to 5,700 ng total PCDFs/ml of spiked feed oil or 4% conversion efficiency (PCBs to PCDFs) was observed for the mineral oil and silicone oil runs.[7] Up to 19,000,000 ng total PCDFs/ml feed oil (19 mg/ml) or 3% conversion efficiency was observed for the askarel fluid.[7] Statistical analysis showed a linear relationship for PCDFs formed versus the amount of PCBs in the feed. Table 27 shows the yields of PCDF homologs from the different runs. Under the optimal conditions, PCDFs are formed from mineral oil or silicone oil contaminated with PCBs at ≥ 5 ppm.

Experiments conducted by Paasivirta *et al.*, provided evidence to support Buser's results that pyrolysis of Aroclor 1254 produces PCDFs. Paasivirta found that the pyrolysis of Aroclor 1254 at 600°C with a 40 ml/minute air stream resulted in 0.16% conversion to PCDFs which is slightly lower but of the same order of magnitude as reported by Buser *et al.*[32] The results of

Table 27. PCDFs Formed in Combustion Studies [7]

RUNS	MonoCDFs (ng)	DiCDFs (ng)	TriCDFs (ng)	TetraCDFs (ng)	PentaCDFs (ng)	HexaCDFs (ng)	HeptaCDFs (ng)	OctaCDF (ng)	PCDFs (ng)
Mineral Oil/	-[a]	-	130	49	NQ[b]	0[c]	-	-	180
5 ppm A-1254	-	-	43	23	0	0	-	-	66
Silicone Oil/	-	-	26	0	90	0	-	-	116
5 ppm A-1254	-	-	31	9	150	0	-	-	190
Mineral Oil/	-	-	200	110	39	8.5	-	-	350
50 ppm A-1254	-	-	140	82	21	2.2	-	-	250
Silicone Oil/	-	-	290	73	62	0	0	0	420
50 ppm A-1254	-	-	530	640	83	0	0	0	1,300
Mineral Oil/	1,700	0	2,200	690	43	7	0	0	4,700
500 ppm A-1254	-	-	1,300	620	170	13	0	0	2,100
(B)	-	-	0	13	0	0	0	0	13
Silicone Oil/	-	-	2,000	740	340	45	-	-	3,100
500 ppm A-1254	50	1,300	5,000	2,100	170	12	0	0	8,600
(B)	0.4	0	0	0	0	0	0	0	0.4
70% A-1254/30%	810	5,100	440,000	1,400,000	6,400,000	910,000	29,000	3,400	9,200,000
Trichlorobenzene	1,900	7,000	220,000	1,100,000	4,700,000	660,000	19,000	1,300	6,700,000
(B)	28	190	310	1,200	17,000	3,000	-	-	22,000
Chlorobenzene Fluid	-	-	2,400	2,600	5,000	0	-	-	9,900
(tri with some tetra)	2,000	29,000	>13,000	>19,000	>22,000	5,200	0	0	>90,000
(B)	-	-	81	25	5	0	-	-	110
Lab Blank	0	0	0	0	0	0	-	-	0

[a] - = Not Analyzed.

[b] NQ = Not Quantitated.

[c] O = Not Detected.

Paasivirta's GC/MS analysis of the phenolic fraction of the PCB pyrolysis product are presented in Table 28.

Table 28. Relative Amounts of PCDFs Formed from PCB (Aroclor 1254) Pyrolysis and Carbon Filter from a Capacitor Fire[32]

ISOMER	PYROLYSIS 500°C	PYROLYSIS 600°C	PYROLYSIS 700°C	CARBON FILTER
Mono-CDF	0.1	0.3	0.1	51.8
Di-CDF	13.7	12.8	5.2	44.3
Tri-CDF	38.8	39.3	29.4	3.9
Tetra-CDF	40.0	35.9	48.7	0
Penta-CDF	7.4	11.0	15.1	0
Hexa-CDF	0	0.8	1.5	0
Total PCDFs	100	100	100	100

The major PCDF homologs identified in the PCB pyrolysis product were (in order of abundance):

- Trichlorodibenzofuran
- Tetrachlorodibenzofuran
- Dichlorodibenzofuran.

Monochlorodibenzofuran and hexachlorodibenzofuran were detected as minor components. The total concentration of PCDFs in the Enso filter was estimated to be 15.8 ppm in carbon. Paasivirta found that chlorinated phenols appear to be an order of magnitude more abundant than PCDFs in capacitor fire products.

In the experiment by Gervason, two askarel fluids were burned in a flame at temperatures ranging from 400°C to 1000°C.[33] The first askarel, Askarel T_1, consisted of 60% PCBs and 40% trichlorobenzenes. The trichlorobenzenes were present in these isomeric forms including: 80% 1,2,4-, 20% 1,2,3-, and < 0.2% 1,2,5-trichlorobenzene. 50 mg of Askarel T_1 was absorbed onto filter paper and burned. The results are presented in Table 29.

Table 29. Concentrations of PCDFs (ppm) Formed from the Burning of Askarel T_1[33]

ISOMER	400°C	500°C	600°C	800°C	1000°C
Tri-CDFs	N.D.[1]	20	400	1.5	N.D.
Tetra-CDFs	5	70	2400	4	N.D.
Penta-CDFs	4	60	1300	5	N.D.

[1]N.D. = Not Detected; detection limit of 0.1 ppm.

The second askarel fluid in Gervason's study, UGILEC T, consisted of 60% UGILEC 141 and 40% trichlorobenzenes (also in the three isomeric forms described above). UGILEC T is primarily dichlorobenzene/dichlorotoluene. No PCDFs were detected from the burning of UGILEC T at temperatures ranging from 400°C to 1000°C with a detection limit of 0.1 ppm.[33]

At the October 1985 PCB Seminar in Seattle, WA, sponsored by the Electric Power Research Institute (EPRI), Rouse presented data on the formation of PCDFs from arcing of PCBs.[34] The study involved the arcing of: (a) a mixture of trichlorobenzene and Aroclor 1254 (1:1 ratio) in oil, (b) Aroclor 1260 in oil, and (c) trichlorobenzene in oil. The results of the first two arcing studies are presented in Tables 30 and 31. Results of the arcing study of trichlorobenzene in oil are presented later in Table 40.

The results indicate that although askarels may contain measurable amounts of PCDFs, arcing does not increase the concentration of PCDFs in the fluid.

Cooke reported on a simulated transformer fire study using retrofill dielectric liquids at the EPRI PCB Seminar.[35] The purpose of this study was to determine the anticipated dioxin or furan level in the event of a PCB transformer fire. Cooke used a combustion chamber (20 inches long x 36 inches wide) with an injection post in the combustion region. Kerosene with 1% silicone was used to set up the nuclei for the catalytic process. The PCBs were injected at 800°C to cascade through the 350-800°C (optimal conditions for PCDF formation) region.

Table 30. PCDF Concentration Before and After Arcing of Aroclor 1254/Trichlorobenzene Mixture (10,000 ppm, 1:1 ratio) in Oil[34]

ISOMER	CONCENTRATION BEFORE ARCING (ppb)	CONCENTRATION AFTER ARCING (ppb)
Tetra-CDFs	367	173
Penta-CDFs	1,850	1,740
Hexa-CDFs	1,790	1,180
Hepta-CDFs	2,960	1,360
Octa-CDF	217	171
Total PCDFs	7,184	4,629

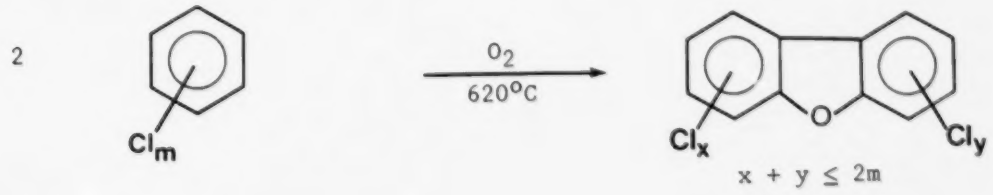
Table 31. PCDF Concentration Before and After Arcing of Aroclor 1260 (10,000 ppm) in Oil[34]

ISOMER	CONCENTRATION BEFORE ARCING (ppb)	CONCENTRATION AFTER ARCING (ppb)
Tetra-CDFs	280	270
Penta-CDFs	2,000	2,500
Hexa-CDFs	1,700	2,000
Hepta-CDFs	930	1,000
Octa-CDF	170	150
Total PCDFs	5,080	5,920

Tests were run using Aroclor 1260, 1254, and 1242 at concentrations of 50 ppm. Theoretically, higher chlorination in the Aroclor should lead to higher levels of PCDFs. Cooke found that the PCDF formation is consistent with this theoretical prediction. The conversion factor for PCBs to PCDFs was 0.0012%-0.003%, which was low under the combustion conditions. The total TCDF concentration ranged from 100-900 ppm.[35]

FORMATION OF PCDFs FROM POLYCHLORINATED BENZENES

PCDFs can be formed in substantial amounts by pyrolysis of chlorobenzenes. In 1979, Buser reported the formation of PCDFs and PCDDs through pyrolytic reactions from chlorobenzenes.[30,36] Table 32 shows the resulting PCDF and PCDD isomers identified in the chlorobenzene pyrolyzate. In these experiments, the pyrolysis of tri-, tetra-, and pentachlorobenzenes, using sealed quartz mini-ampoules at 620°C in the presence of air, yielded tetra- to octa-CDF.



Significant quantities of PCDFs were found in most of the pyrolyzed samples (see Table 33). The likelihood of formation of PCDFs is highly dependent on the concentration of chlorobenzenes in the reaction system.

As seen in Table 33, significant quantities of PCDFs were formed from the tri- and tetrachlorobenzenes, and from the combined chlorobenzene sample. In general, the PCDFs formed had chlorine numbers of 2m-2, 2m-1, and 2m, where m is the number of chlorine atoms on the reacting chlorobenzene. With the trichloro- benzenes, some higher chlorinated dibenzofurans (hepta-CDF) were also observed; presumably, they are formed from higher chlorinated benzenes produced during pyrolysis.

The optimal temperature for the conversion to PCDFs seems to be 500-600°C. At temperatures exceeding 600-700°C, the degradation of PCDDs and PCDFs takes place at a faster rate than the rate of formation. In addition to the temperature, the retention time is an important parameter. The experimental results are summarized in Table 34.

Table 32. Identification of PCDF and PCDD Isomers in the Combined Chlorobenzene Pyrolyzate[30,36]

PCDF ISOMER	PCDD ISOMER
1,3,6,8-Tetra-CDF	1,3,6,8-Tetra-CDD
1,3,7,9-Tetra-CDF	1,3,7,9-Tetra-CDD
1,3,6,7-Tetra-CDF	1,3,7,8-Tetra-CDD
1,2,4,6-Tetra-CDF	1,3,6,7-Tetra-CDD
2,4,6,8-Tetra-CDF	2,3,7,8-Tetra-CDD
2,3,6,8-Tetra-CDF	1,3,8,9-Tetra-CDD
2,3,7,8-Tetra-CDF	1,2,7,8-Tetra-CDD
1,2,4,6,8-Penta-CDF	1,2,4,6,8-Penta-CDD (or 1,2,4,7,9-)
1,3,4,7,9-Penta-CDF	1,2,3,6,8-Penta-CDD
1,3,4,7,8-Penta-CDF	1,2,4,7,8-Penta-CDD
1,2,4,7,8-Penta-CDF	1,2,3,7,9-Penta-CDD
1,2,4,7,9-Penta-CDF	1,2,3,7,8-Penta-CDD
1,2,3,7,8- and 1,2,3,4,8-Penta-CDF	1,2,3,6,7-Penta-CDD
1,2,3,6,7-Penta-CDF	1,2,3,8,9-Penta-CDD
1,2,6,7,8-Penta-CDF	
1,3,4,8,9-Penta-CDF	
2,3,4,6,8-Penta-CDF	
1,2,4,8,9-Penta-CDF	
2,3,4,7,8-Penta-CDF	
2,3,4,6,7-Penta-CDF	
1,2,3,4,6,8-Hexa-CDF	1,2,4,6,7,9-Hexa-CDD (or 1,2,4,6,8,9-)
1,3,4,6,7,8-Hexa-CDF	1,2,3,4,6,8-Hexa-CDD
1,2,4,6,7,8-Hexa-CDF	1,2,3,6,8,9-Hexa-CDD-(or 1,2,3,6,7,9-)
1,2,3,4,7,8-Hexa-CDF	1,2,3,4,7,8-Hexa-CDD
1,2,3,6,7,8-Hexa-CDF	1,2,3,6,7,8-Hexa-CDD
1,2,4,6,8,9- and 1,2,3,4,6,7-Hexa-CDF	1,2,3,7,8,9-Hexa-CDD
1,2,3,6,8,9-Hexa-CDF	1,2,3,4,6,7-Hexa-CDD
2,3,4,6,7,8-Hexa-CDF	
1,2,3,4,6,7,8-Hepta-CDF	1,2,3,4,6,7,9-Hepta-CDD
1,2,3,4,6,7,9-Hepta-CDF	1,2,3,4,6,7,8-Hepta-CDD
1,2,3,4,6,8,9-Hepta-CDF	
1,2,3,4,7,8,9-Hepta-CDF	
Octa-CDF	Octa-CDD

Table 33. Formation of PCDFs from the Pyrolysis of Chlorobenzenes[30,36]

COMPOUND(S)	PCDFs FORMED (ng/sample)				
	TETRA-	PENTA-	HEXA-	HEPTA-	OCTA-
Trichlorobenzenes[a]	400	1100	550	50	< 5
Tetrachlorobenzenes[b]	< 2	5	160	450	200
Pentachlorobenzene[c]	< 2	< 5	< 5	5	30
Combined chlorobenzenes[d]	80	600	1100	600	60

[a]200 mcg total with equal amounts of 1,2,3-, 1,2,4-, and 1,3,5-trichlorobenzene.

[b]200 mcg total with equal amounts of 1,2,3,4-, 1,2,3,5-, and 1,2,4,5-tetrachlorobenzene.

[c]200 mcg pentachlorobenzene.

[d]500 mcg total with equal amounts of all tri-, tetra-, and pentachlorobenzenes (7 compounds).

Table 34. Summary of Formation of PCDFs from the Pyrolysis of Chlorobenzenes[30,36]

COMPOUND(S) PYROLYZED	PCDFs YIELD
1,2,3-, 1,2,4-, and 1,3,5-Trichlorobenzene	1%[a]
1,2,3,4-, 1,2,3,5-, and 1,2,4,5-Tetrachlorobenzene	0.4%[b]
Pentachlorobenzene	0.02%

[a]tetra-CDFs 0.2%
penta-CDFs 0.5%
hexa-CDFs 0.3%

[b]hexa-CDFs 0.1%
hepta-CDFs 0.2%
octa-CDF 0.2%

Further evidence to support the formation of PCDFs from the pyrolysis of chlorobenzenes can be found in the results of the Midwest Research Institute study.[7] As mentioned earlier, this study included the pyrolysis of trichlorobenzene dielectric fluid at 675°C for 8 seconds with 8% excess oxygen. Up to 110,000 ng total PCDFs/ml feed oil (> 0.004% yield) was observed for the trichlorobenzene runs. These results, presented in Table 27, support earlier laboratory data and analytical results of soot material from transformer and capacitor fires.

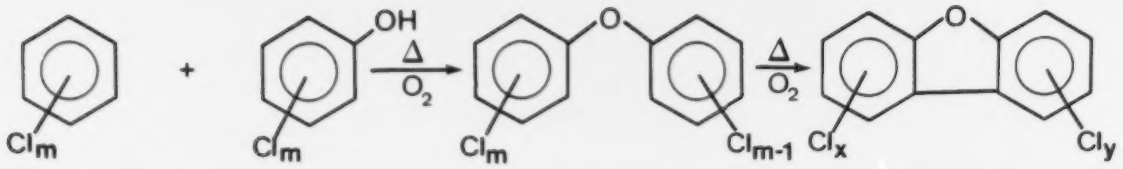
Paasivirta *et al.*, studied the pyrolysis of a trichlorobenzene/PCB mixture. The details of this study were described in this section, and the relative amounts of PCDFs formed from the pyrolysis of the mixture were presented in Table 28.[32]

The study conducted by Gervason, described earlier in this section, provides evidence in support of the formation of PCDFs from trichlorobenzenes. This study indicates that the burning of a 60% PCB/40% trichlorobenzene mixture results in the formation of PCDFs.[33] The results were presented in Table 29.

FORMATION OF PCDFs FROM CHLOROPHENOLS

In Buser's experiments, the pyrolysis of chlorobenzenes yielded a series of chlorinated compounds including PCDFs, PCDDs, chlorophenols, and in some cases PCBs, polychlorinated naphthalenes, and polychlorinated styrenes.[30,36] All pyrolyzed samples showed the presence of chlorophenols. Buser suggested that these chlorophenols could possibly serve as reaction intermediates in the formation of PCDFs from chlorobenzenes. A reaction of chlorophenol with unreacted chlorobenzene could lead to the formation of polychlorinated diphenyl ethers (PCDPE), which are known to form PCDFs upon pyrolysis.[30,36,37]

Test burns of pentachlorophenol (PCP) waste were performed in a U.S. industrial boiler. Baghouse ash and bottom ash were analyzed and results are presented in Table 35. The total level of PCDFs in the baghouse ash was 2.9 mcg/g.[37]



PCDPE PCDF

Table 35. Levels of PCDFs from Burning of Pentachlorophenol-Contaminated Waste[37]

CONTAMINANT	BAGHOUSE ASH (ppm)	BOTTOM ASH (ppm)
Tetra-CDFs	0.90	N.D.[a]
2,3,7,8-Tetra-CDF	0.10	N.D.
Penta-CDFs	1.5	N.D.
1,2,3,7,8-Penta-CDF	0.05	N.D.
2,3,4,7,8-Penta-CDF	0.10	N.D.
Hexa-CDFs	0.15	N.D.
1,2,3,4,7,8-Hexa-CDF	0.02	N.D.
Hepta-CDFs	0.06	N.D.
Octa-CDF	0.006	N.D.

[a]N.D. = Not Detected.

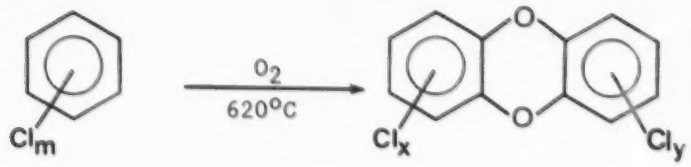
FORMATION OF PCDDs FROM PCBs

There is no experimental evidence for PCDD formation from pyrolysis of PCBs, and theoretical considerations indicate that this conversion does not occur. The thermolysis of PCBs yields exclusively PCDFs with no PCDDs detected.[14]

FORMATION OF PCDDs FROM POLYCHLORINATED BENZENES

Buser has reported that PCDDs are formed from the pyrolysis of chlorobenzenes.[30,36] The pyrolyses of tri- and tetrachlorobenzenes and pentachlorobenzene were carried out in sealed quartz mini-ampoules at 620°C in the presence of air. Analysis of the pyrolyzates revealed the presence of chlorobenzenes, PCDDs, PCDFs, chlorophenols, and in some cases PCBs, polychlorinated naphthalenes, and polychlorinated styrenes.

As seen in Table 36, substantial amounts of PCDDs (hexa-, hepta-, and some octa-CDD) were observed from the tetrachlorobenzenes and from the combined chlorobenzene sample (tetra- to hepta-CDDs). Smaller quantities of tetra- and penta-CDDs were obtained from the trichlorobenzenes, while pentachlorobenzene yielded only an insignificant amount of octa-CDD.



The formation of these tricyclic aromatic compounds is bimolecular; the likelihood of this formation is highly dependent on the concentration of chlorobenzenes in the reaction system.[36] The optimal temperature for the conversion of chlorobenzenes to PCDDs seems to be 500-600°C. The results presented in Table 37 support the previous evidence that chlorobenzenes are converted to PCDDs during pyrolysis.

The Midwest Research Institute study, conducted under contract with EPA, also provided data concerning the pyrolysis of trichlorobenzene dielectric fluid.[7] The pyrolysis of a non-PCB askarel fluid, containing mostly trichlorobenzenes with some tetrachlorobenzenes, yielded up to 1,900 ng total PCDDs/ml feed oil (0.0001% yield). These results, presented in Table 38, support previous laboratory data and analytical results of soot material from

Table 36. Formation of PCDDs from the Pyrolysis of Chlorobenzenes[30,36]

COMPOUND(S)	PCDDs FORMED (ng/sample)				
	TETRA-	PENTA-	HEXA-	HEPTA-	OCTA-
Trichlorobenzenes[a]	30	20	< 5	< 5	< 5
Tetrachlorobenzenes[b]	< 2	5	140	160	30
Pentachlorobenzene[c]	< 2	< 5	< 5	< 5	5
Combined chlorobenzenes[d]	50	220	220	70	5

[a]200 mcg total with equal amounts of 1,2,3-, 1,2,4-, and 1,3,5-trichlorobenzene.

[b]200 mcg total with equal amounts of 1,2,3,4-, 1,2,3,5-, and 1,2,4,5-tetrachlorobenzene.

[c]200 mcg pentachlorobenzene.

[d]500 mcg total with equal amounts of all tri- and tetrachlorobenzenes, and pentachlorobenzene (7 compounds).

Table 37. Summary of Formation of PCDDs from the Pyrolysis of Chlorobenzenes[30,36]

COMPOUND(S) PYROLYZED	PCDD YIELD
1,2,3-, 1,2,4-, and 1,3,5-Trichlorobenzene	0.025%
1,2,3,4-, 1,2,3,5-, and 1,2,4,5-Tetrachlorobenzene	0.15%
Pentachlorobenzene	0.002%

Table 38. PCDDs Formed in Combustion Studies (7)

RUNS	MonoCDD (ng)	DiCDD (ng)	TriCDD (ng)	TetraCDD (ng)	PentaCDD (ng)	HexaCDD (ng)	HeptaCDD (ng)	OctaCDD (ng)	PCDDs (ng)
Silicone Oil/	-	-	0	0	7.7	0	-	-	7.7
500 ppm Aroclor 1254	0	0	0	0	1.7	0	0	0	1.7
70% Aroclor 1254/	0	0	0	0	0	0	330	37	360
30% Trichlorobenzene	0	0	0	0	0	0	230	51	280
Chlorobenzene Fluids	-	-	1,100	440	0	0	-	-	1,500
(mostly tri with some tetra)	0	0	630	520	0	72	0	0	1,200

transformer and capacitor fires, which determined that chlorobenzenes are required for PCDD formation.

As discussed earlier in this section, Paasivirta *et al.*, studied the pyrolysis of a mixture of Aroclor 1254 and chlorobenzenes. Such mixtures usually contain anywhere from 13% to 60% trichlorobenzene and sometimes tetrachlorobenzene.[32] The results of the GC/MS analysis indicated that PCDDs were present in the pyrolysis product. Table 39 gives the relative amounts of PCDDs formed from pyrolysis of this PCB/chlorobenzene mixture.

Table 39. Relative Amounts of PCDDs Formed from Analysis of a PCB/Chlorobenzene Mixture[32]

ISOMER	PYROLYSIS 500°C (%)	PYROLYSIS 600°C (%)	PYROLYSIS 700°C (%)
Di-CDD	17.2	0.7	4.6
Tri-CDD	10.0	18.4	13.6
Tetra-CDD	72.9	57.0	66.3
Penta-CDD	0	24.1	17.4
Total PCDDs	100	100	100

The major PCDDs detected in the pyrolysis product were tetra-CDD (highest concentration) and penta-CDD. The pyrolysis of the Aroclor 1254 mixture resulted in a 0.16% conversion to PCDDs, which is lower than Buser's estimate but of the same order of magnitude.[32]

Paasivirta found high amounts of polychlorophenols and polychlorinated biphenyls in the pyrolysis products of the PCB mixture and a capacitor fire.[32]

As discussed earlier, Rouse presented data at the 1985 EPRI PCB Seminar in Seattle, WA, on the formation of PCDDs from arcing of trichlorobenzene in oil.[34] The PCDD concentrations resulting from this arcing study are presented in Table 40.

Table 40. PCDD Concentration Before and After Arcing of Trichlorobenzene (10,000 ppm) in Oil[34]

ISOMER	CONCENTRATION BEFORE ARCING (ppb)	CONCENTRATION AFTER ARCING (ppb)
Tetra-CDD	N.D.[a]	N.D.
Penta-CDD	0.4	N.D.

[a]N.D. = Not Detected.

Gervason's study, previously described in this section, indicated the formation of PCDDs from Askarel T_1 (60% PCB/40% trichlorobenzenes mixture). The results are presented in Table 41.

Table 41. Concentrations of 2,3,7,8-TCDD Formed from the Burning of Askarel T_1[33]

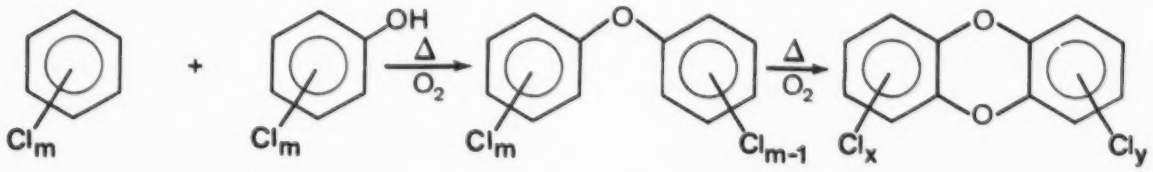
TEMPERATURE (°C)	2,3,7,8-TCDD CONCENTRATION (ppm)
400	1.5
500	1.0
600	15
800	0.1
1000	0.15

FORMATION OF PCDDs FROM CHLOROPHENOLS

While investigating the pyrolysis products of chlorobenzenes, Buser found that chlorophenols were present in all of the pyrolyzed chlorobenzene samples.[30,36] These chlorophenols could possibly serve as reaction intermediates in the formation of PCDDs from chlorobenzenes. A reaction of chlorophenol with unreacted chlorobenzene could lead to the formation of

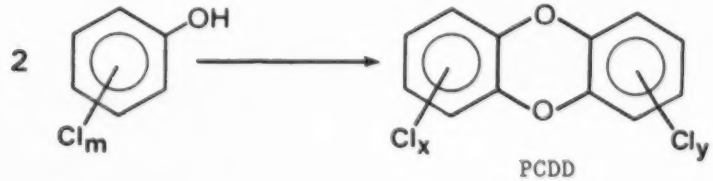
polychlorinated diphenyl ethers (PCDPEs), which are known to form PCDDs upon pyrolysis.[30,36]

Rappe *et al.*, reported PCDD formation from the burning of chlorophenols.[38] Two of the most commonly used chlorophenol formulations on the Scandinavian market, Servarex Teknish (Gullviks Fabrinks AB, Malmo, Sweden, lot Npnr 524) and Kymmene KY-5 (Kymmene OY, Kuusankoski, Finland; lot 132/16), were used. These formulations contain approximately 5% of 2,4,6-tri-, 50% of 2,3,4,6-tetra-, and 10% of pentachlorophenol in their sodium salt form. The levels of PCDDs found in the two formulations are similar.



PCDPE PCDD

Another route of PCDD formation involves the dimerization of chlorophenols, although the condensation via PCDPEs may be preferred.



PCDD

Test burns of pentachlorophenol waste were performed in an industrial boiler in the U.S. Samples of baghouse ash and bottom ash were analyzed and results are reflected in Table 42. In the baghouse ash the total level of PCDDs was found to be 5.3 ppm. Lower chlorinated PCDDs predominated. In the bottom ash, the higher chlorinated PCDDs were found in greater amounts.[37,38]

Table 42. Levels of PCDDs from Burning of Pentachlorophenol-Contaminated Waste[37]

CONTAMINANT	BAGHOUSE ASH (ppm)	BOTTOM ASH (ppm)
Tetra-CDDs	0.96	0.01
2,3,7,8-Tetra-CDD	< 0.005	< 0.001
Penta-CDDs	1.4	0.02
Hexa-CDDs	2.0	0.04
Hepta-CDDs	0.7	0.10
Octa-CDD	0.2	0.14

SECTION 5

CONTAMINATION SITUATIONS INVOLVING PCDDs FROM PCBs AND CHLOROBENZENES

This section reports some situations of facility contamination by PCDDs, generated from thermal processes involving chlorobenzenes and/or polybrominated biphenyls. As discussed earlier, under the proposed rules for restricting hazardous waste in landfills, PCDDs-contaminated sites will be subject to substantially more stringent cleanup and diposal regulations. The following serves to highlight examples of contamination situations where such regulations might apply.

PCDD FORMATION FROM 1,2,4-TRICHLOROBENZENE FEEDSTOCK FROM LINDANE PRODUCTION

A European manufacturing process for trichlorobenzene provides further evidence of dioxin contaminant formation from chlorobenzene. This process converts lindane manufacturing wastes (α, β, δ -hexachlorocyclohexane, HCCH) to predominantly (70-75%) 1,2,4-trichlorobenzene, which, after purification, is transformed to 1,2,4,5-tetrachlorobenzene (used as the feedstock for 2,4,5-trichlorophenol). The process involved the low temperature (200-240°C) pyrolysis of the lindane wastes with a carbon catalyst using indirect heating of a closed reaction mantle. The residues from both the mantle and the trichlorobenzene still were analyzed by Buser in Switzerland. The results of this analysis are presented in Table 43.

Extreme care should be taken when pyrolyzing and/or distilling chlorinated aromatics to exclude air (oxygen) from the syste so that undesirable chlorinated contaminants, including PCDDs, will not be formed.

PCDDs FORMATION FROM A PITTSBURGH AREA METAL RECLAIMING FACILITY

PCDDs and PCDFs have also been found at active/inactive scrap metal reclaiming facilities, where PCB transformer and capacitor units are processed for their respective copper values. One such example in the Pittsburgh, PA, area is a 1/2-acre site in the midst of a residential community, with about

1,000 persons within a 1/4-mile radius. This site includes a commercial building containing a small incinerator that was used not only to combust PCBs, but also to provide heat to the surrounding area. In August 1982, NIOSH conducted an inspection and detected 8 ppm octa-CDD in a sample of soil taken at a depth of 1 foot near the PCB liquid storage area. In April 1984, EPA Region III staff removed and analyzed dust samples from inside the building, the results of which are shown in Table 44.

As a result, an Immediate Removal Action was initiated on May 29, 1984. An extension survey demonstrated that the dioxin/furan contamination was restricted to the interior of the incinerator building. More than 5,000 tons of PCB-contaminated soil, containing ≥ 50 ppm PCBs, were excavated, loaded, and transported for disposal to the CECOS facility in Niagara Falls, NY, before the RCRA Dioxin Listing Rule went into effect (on July 15, 1985). Scrape samples from interior building surfaces showed:

Tetra-CDDs	10-94 ng/g or ppb
Tetra-CDFs	38-615 ng/g or ppb

Sixty transformer casings remain on site today. The estimated cost for the disposition of the remaining contaminated materials (i.e., PCBs, PCDDs, and PCDFs) and security of the site on a temporary or interim basis is $2.885 million -- for a 1/2-acre site.

PCDD AND PCDF FORMATION FROM STRANDLEY METAL RECOVERY SITE, PURDY, WA

Strandley Scrap Metal occupies 65 acres, including 1 to 2 acres of open work areas, along Highway 302 east of Purdy, WA. The Strandley/Manning site contains several buildings/warehouses, an 8,000 gallon storage tank (old railroad tank car), transformer casings, a large wire pile, scrap metal, old forklifts, and several drums. Transformer salvage operations occurred at the site between 1972 and 1983. Some materials may have been burned at the site.(41)

The Strandley/Manning Property site is known to contain PCBs contamination in the soil and some remaining containers, and there is evidence of offsite

Table 43. Dioxin Isomers from Pyrolyzed HCCH Residues and Trichlorobenzene Stillbottoms[39]

DIOXIN ISOMER	CONCENTRATION (ppm)
Tetra-CDDs	12
2,3,7,8-Tetra-CDD	0.3
Penta-CDDs	200
1,2,3,7,8-Penta-CDD	7
Hexa-CDDs	680
1,2,3,4,7,8-Hexa-CDD	45
1,2,3,6,7,8-Hexa-CDD	150
1,2,3,7,8,9-Hexa-CDD	65
1,2,3,4,6,7,9-Hepta-CDD	1,400
1,2,3,4,6,7,8-Hepta-CDD	3,000
Octa-CDD	7,600

Table 44. Dioxin and Furan in Dust from Pittsburgh Area Metal Reclaiming Facility[40]

HOMOLOG	CONCENTRATION (ppb)
Tetra-CDDs	17-59
2,3,7,8-Tetra-CDD	0.79-2.5
Tetra-CDFs	413-1232
2,3,7,8-Tetra-CDF	74-241

contaminant migration. Dioxins and furans have also been detected, possibly as a result of past burning of oil and transformer windings.

Prior to the sampling for a preliminary site assessment, EPA had already performed some sampling. PCBs were found in the storage tank, in soils, and in stream sediments. Very low levels of PCBs were found in the shellfish and sediments of nearby Burley Lagoon. Results of swab sampling of onsite equipment indicated some PCBs contamination. Also, 2,3,7,8-TCDD was found in a stove used to burn PCBs-contaminated oil. The presence of several other dioxin and furan isomers has also been detected. Limited excavation of soils with high levels of PCBs near the old storage tank location resulted in finding significant PCBs contamination at a depth of 6 feet.

The following analyses were perfomed on the various samples:

- PCBs (for soil, sediment, drum, and swab samples)
- PCDDs/PCDFs (for some soil and swab samples)
  - Total PCDDs
  - Total PCDFs
  - 2,3,7,8-TCDD
  - 2,3,7,8-TCDF
  - All tetra- through octa-CDDs (total homologs, not isomer-specific)
  - All tetra- through octa-CDFs (total homologs, not isomer-specific)
- Halogenated Organics.

A summary of sample results for PCBs analysis is presented in Tables 45 and 46.

Table 45. Summary of Sample Results from Strandley Scrap Metal Site[41]

SAMPLE MEDIA	PCB CONCENTRATION (ppm)[a]
Soil	136
Soil	27
Soil	37
Soil	1200
Oil Sludge	5600 (wet basis)
Soil	37
Soil	63
Soil	28
Soil	230
Soil	46 (plus 49 of Aroclor 1242)
Soil	62 (plus 10 of Aroclor 1242)
Soil	73
Soil	58 (51 duplicate)
Oil	120 (wet basis)
Soil	162
Residue	4.4
Soil	99
Soil	30
Soil	26
Sediment	88
Sediment	4.7
Water	2.47 mcg/l
Soil	190
Soil	4.6
Soil	91 (Aroclor 1254)
Soil	71
Empty Sample Bottle	N.D.[b]
Water - Transfer blank	0.069 mcg/l Aroclor 1254
Water - Transport blank	0.42 mcg/l Aroclor 1254

[a]PCB concentration is in units of mcg/g (ppm) of Aroclor 1260 on a dry weight basis unless otherwise stated.

[b]N.D. = Not Detected.

Table 46. Summary of Sample Results from Strandley Site and Burley Lagoon[41]

SAMPLE MEDIA	DESCRIPTION	PCB CONCENTRATION (ppm)[a]
Tissue	Shellfish sample	0.051 (wet basis)
Water		1.5 ppb
Sediment		2.6
Sediment		15.3
Sediment		0.43
Sediment		0.51
Sediment		0.026
Sediment		0.072
	Transport blank	N.D.[b] (0.04 ppb)
	Sediment blank	N.D. (0.001)
	Transport blank	N.D. (0.03 ppb)
Sediment	Stream near mouth, 40' up from tree line	67
Water	Stream near mouth, 40' up from tree line	0.68 ppb
Sediment	Stream about 140' up from tree line	88
Sediment	Stream 20' downstream from culvert below pond	302
Water	Stream 20' downstream from culvert below pond	0.69 ppb
Sediment	Sediment from spring	0.102
Water	House 1/2 gallon clear	N.D. (0.02 ppb)
Water	House 1/2 gallon amber	N.D. (0.02 ppb)
Water	Spring 1/2 gallon clear	N.D. (0.02 ppb)
Water	Spring 1/2 gallon amber	N.D. (0.02 ppb)
Water	Transport blank 1/2 gallon clear	N.D. (0.02 ppb)
Water	Transfer blank 1/2 gallon clear	N.D. (0.02 ppb)
Water	Transport blank 1/2 gallon amber	N.D. (0.02 ppb)
Water	Transfer blank 1/2 gallon amber	N.D. (0.02 ppb)
Sediment	South side access road to Strandley yard, composite of two samples	45
Sediment	North side access road to Strandley yard, composite of two samples	178
Sediment	Auto body yard, composite of four samples	56
Oil	Lift truck hydraulic reservoir	N.D. (1.0)
	Oily rag on lift truck	13
Sediment	Stream sediment by drain west of pond	93
Sediment	Spring composite below yellow bus	6.3
Sediment	Driveway parking lot by Willow Road, composite of four samples	4.5
	Sediment blank	N.D. (1.0)

[a]Units are in ppm (mcg/g) dry weight of Aroclor 1260 unless otherwise specified.

[b]N.D. = Not Detected; value in parentheses is the minimum quantifiable limit.

Table 46. Summary of Sample Results from Strandley Site and Burley Lagoon (Continued)

SAMPLE MEDIA	DESCRIPTION	PCB CONCENTRATION (ppm)[a]
Sediment	Station #1	0.0100
Sediment	Station #1	0.02044
Sediment	Station #2	N.D.[b] (0.01)
Sediment	Station #2	N.D. (0.01)
Sediment	Station #3	0.019
Sediment	Station #4	N.D. (0.010)
Sediment	Station #5	0.026
Sediment	Station #6	0.36
Sediment	Station #7	N.D. (0.010)
	Sediment Blank	N.D. (0.010)
Tissue	Raft Culture Pacific Oysters	0.082 (wet basis)
Tissue	Mid-Bay Touging Pacific Oysters	0.145 (wet basis)
Tissue	West Beach Japanese Little Necks	N.D. (0.016) (wet basis)
Tissue	South Beach Japanese Little Necks	0.016 (wet basis)
Tissue	Plant Site Pacific Oysters	0.11 (wet basis)
Tissue	Northeast Lagoon Macoma Clams	0.048 (wet basis)
Tissue	Northeast Lagoon Ghost Shrimp	0.26 (wet basis)
Tissue	Northwest Lagoon Macoma Clams	0.053 (wet basis)
Tissue	North Lagoon Ghost Shrimp	0.78 (wet basis)
Tissue	North Lagoon Small Clams	0.49 (wet basis)
Sediment	Station #8	0.034
Sediment	Station #9	0.047
Sediment	Station #10	0.055
Sediment	Station #11	0.061
Sediment	Station #12	0.035
Sediment	Station #13	0.047
Sediment	Station #14	0.078
Sediment	Station #15	18.1
Sediment	Station #16	40
Sedmient	Station #17	16.2
Sediment	Station #18	3.1
Sediment	Station #19	0.25
Sediment	Station #20	0.45
Sediment	Station #21	0.24
Sediment	Station #22	0.365
Water	Water transfer blank	N.D. (0.01 ppb)
Water	Water transport blank	N.D. (0.01 ppb)
	Sediment blank	N.D. (0.01)
Water	Station #15	5.16 ppb

[a]Units are in ppm (mcg/g) dry weight of Aroclor 1260 unless otherwise specified.

[b]N.D. = Not Detected; value in parentheses is the minimum quantifiable limit.

California Analytical Laboratories analyzed numerous soil samples from the Strandley Site. The results of their analyses are presented in Table 47.

Table 47. PCDD/PCDF Analysis of Soil Samples From Strandley Site[41]

SAMPLE	ISOMER	CONCENTRATION (ng/g or ppb)
1	Hepta-CDF	0.96
2	2,3,7,8-Tetra-CDF	0.16
	Total Tetra-CDFs	0.23
3	None	N.D.[a]

[a]N.D. = Not detected.

Samples from four different areas of the site were also analyzed for PCDDs/PCDFs by California Analytical Laboratories. Table 48 gives the concentration of PCDDs/PCDFs detected in these different samples.

Table 48. PCDD/PCDF Analysis of Various Samples from Strandley Site[42]

SAMPLE DESCRIPTION	ISOMER	CONCENTRATION (ppb)
Sample of Burn Area from Under Container	Octa-CDD	8.7
Sample of Ash on Bank of Roadway	2,3,7,8-Tetra-CDF	3.5
	Total Tetra-CDFs	13
	2,3,4,7,8-Penta-CDF	4.7
	Total Penta-CDFs	62
	1,2,3,4,7,8-Hexa-CDF	38
	1,2,3,7,8,9-Hexa-CDF	14
	2,3,4,6,7,8-Hexa-CDF	1.7
	Total Hexa-CDFs	91

Table 48. PCDD/PCDF Analysis of Various Samples from Strandley Site (Continued)

SAMPLE DESCRIPTION	ISOMER	CONCENTRATION (ppb)
	1,2,3,4,6,7,8-Hepta-CDF	90
	Total Hepta-CDFs	90
	Octa-CDF	55
	Total Tetra-CDDs	N.D.[a]
	Total Penta-CDDs	4.2
	Total Hexa-CDDs	1.8
	1,2,3,4,6,7,8-Hepta-CDDs	12
	Total Hepta-CDDs	25
	Octa-CDD	43
Sample of Ash from Stove in Shop.	2,3,7,8-Tetra-CDF	160
	Total Tetra-CDFs	545
	1,2,3,7,8-Penta-CDF	81
	2,3,4,7,8-Penta-CDF	110
	Total Penta-CDFs	2000
	1,2,3,4,7,8-Hexa-CDF	730
	1,2,3,7,8,9-Hexa-CDF	530
	2,3,4,6,7,8-Hexa-CDF	38
	Total Hexa-CDFs	2300
	1,2,3,4,6,7,8-Hepta-CDF	1500
	Total Hepta-CDFs	2000
	Octa-CDF	320
	Total Tetra-CDDs	178
	1,2,3,7,8-Penta-CDD	21
	Total Penta-CDDs	845
	1,2,3,4,7,8-Hexa-CDD	71
	Total Hexa-CDDs	1100

[a]N.D. = Not Detected.

[b]Isomers co-elute.

Table 48. PCDD/PCDF Analysis of Various Samples from Strandley Site (Continued)

SAMPLE DESCRIPTION	ISOMER	CONCENTRATION (ppb)
	1,2,3,4,6,7,8-Hepta-CDD	740
	Total Hepta-CDDs	2000
	Octa-CDD	890
Sample of Ash from the Woods	2,3,7,8-Tetra-CDF	3.2
	Total Tetra-CDFs	9.7
	Total Penta-CDFs	19.0
	1,2,3,4,7,8-Hexa-CDF	24.0[b]
	1,2,3,6,7,8-Hexa-CDF	24.0[b]
	1,2,3,7,8,9-Hexa-CDF	6.8
	Total Hexa-CDFs	52.0
	1,2,3,4,6,7,8-Hepta-CDF	37.0
	Total Hepta-CDFs	37.0
	Octa-CDF	15.0
	Total Tetra-CDDs	2.5
	Total Penta-CDDs	N.D.
	Total Hexa-CDDs	2.2
	1,2,3,4,6,7,8-Hepta-CDD	4.5
	Total Hepta-CDDs	10.0
	Octa-CDD	25.0

[a]N.D. = Not Detected.

[b]Isomers co-elute.

SECTION 6

ANALYSIS AND EVALUATION

In the aftermath of a PCB transformer fire, the usual immediate action is to analyze the soot generated in the fire for toxic combustion products formed in order to assess the immediate health risk that may be present in the building or facility. Much has been learned over the last few years from investigating the PCB transformer fire incidents that have occurred throughout western Europe and the United States. The issues that the research community has focused on appear to be following:

- Are PCDDs and PCDFs formed in PCB transformers under normal operating conditions?
- How are the constituents of the transformer fluids related to the type and amount of PCDDs and PCDFs formed?
- What are the temperature and other environmental conditions that favor the formation of the PCB combustion products?

Answers to such questions are necessary to properly assess PCB transformer fire incidents and to develop appropriate emergency response and longer term remedial measures. This section of the report addresses these questions by correlating, analyzing, and evaluating the data presented in the earlier sections.

COMPARISON OF A PCB TRANSFORMER FIRE WITH THE INCINERATION SITUATION

The combustion products resulting from PCB fires are a function of many variables including:

- Carbon-to-hydrogen ratio.
- Chlorine content or weight percentage chlorine.
- Type of contaminants.
- Reaction (fire) temperature.
- Residence time of reactants (air and fuel).
- Turbulence or mixing efficiency of fuel and air.
- Atmospheric versus reduced oxygen environment.

The combustion and molecular decomposition of chemicals in a PCB transformer fire is not unlike that of the combustion situation in the incineration of chlorinated substances. The general equation for complete combustion of chlorinated hydrocarbons during incineration can be written as:

1) $C_aH_bCl_c + pO_2 + 3.78\ pN_2 + mH_2O \longrightarrow$

$3.78\ pN_2 + (m + n/2)\ H_2O + aCO_2 + (b - n)\ HCl$

$+ 1/2(n + c - b)\ Cl_2 + (p - a - n/4)\ O_2 + Qkcal.$

The atoms of chlorine will be distributed between HCl on one hand, and stable chlorine molecules on the other hand. This is consistent with DEACON equilibrium in the furnace's core, after proper combustion. The equilibrium state is reached with a kinetic of each partial reaction, different from the one of proper combustion reactions.

This equilibrium state can be written as:

2) $4\ HCl + O_2 \underset{II}{\overset{I}{\rightleftharpoons}} 2\ H_2O + 2\ Cl_2 - 20.8$ kcal (exothermic)

If mH_2O, nCl_2, oO_2, qHCl, and N are the number of molecules of water, chlorine, oxygen, and hydrochloric acid, and the total number of molecules in the combustion gases, respectively, the equilibrium constant, in the average conditions of a homogeneous furnace, is:

$$Kp = \frac{N}{p} \frac{(mH_2O)^2 \times (nCl_2)^2}{(oO_2) \times (qHCl)^4}$$

which is defined using the coefficients of equation I. Kp is related to the temperature by the formula:

3) $$\log Kp = \frac{6034}{T} - 6.97$$

where $T = {}^oK$

The goal is to displace to a maximum the equilibrium (2) to the left. Considering the equilibrium (2) and equation (3), it can be seen that, in order

to decrease the chlorine's partial pressure in the gases after combustion, the following conditions have to be fulfilled:

- A high temperature of combustion.
- A furnace designed in such a way that the residence time of the gases at the high temperature is large enough to enable DEACON's equilibrium and complete combustion to take place.
- A water vapor partial pressure that is as large as possible, taking into account the thermal and water balances of the system.
- A very efficient "quench" device to "freeze" the above-said equilibrium.

A PCB transformer fire, however, is not a controlled combustion situation such as that in an incineration furnace; but it can be assumed that at the point of combustion, the thermal properties of the transformer fluids (vapor pressure, enthalpies and entropies, etc.) and generated products will determine the type of combustion and products generated. Unfortunately, because of their high toxicity, the thermal properties of many PCDFs, PCDDs, and other toxic chlorinated combustion products have not been measured.

Rordorf recently developed an approach to estimate the vapor pressure, boiling point, and other thermal properties of toxic substances such as chlorinated dioxins.[42] The scheme is shown in Figure 1.

Vapor pressures of liquids of known freezing and boiling points can be predicted by equation VII, where K is from equation V. Equation VII can also be used to estimate boiling points if the melting points and vapor pressures at T_m are known for given compounds. Equation VII is first used to predict boiling points of the investigated chlorodioxins and furans.

The enthalpies of fusion need to be known for the projection of solid vapor pressure curves from (predicted) liquid vapor pressure data. The Gibbs free energies and enthalpies of sublimation equal the sums of the corresponding functions of fusion plus melting (VIII and IX). Equation XI, which is obtained from VIII, IX, and X, states that similar sums hold for the entropies. The entropies of fusion at T_m equal the enthalpies of fusion divided by the melting temperatures (XIII) as the Gibbs free energies of fusion are zero at T_m. The

Figure 1. Relationship Between the Vapor Pressures of the Solid and Liquid Phases at Temperatures T, the Melting Point (T_m), and the Boiling Point (T_b) [42]

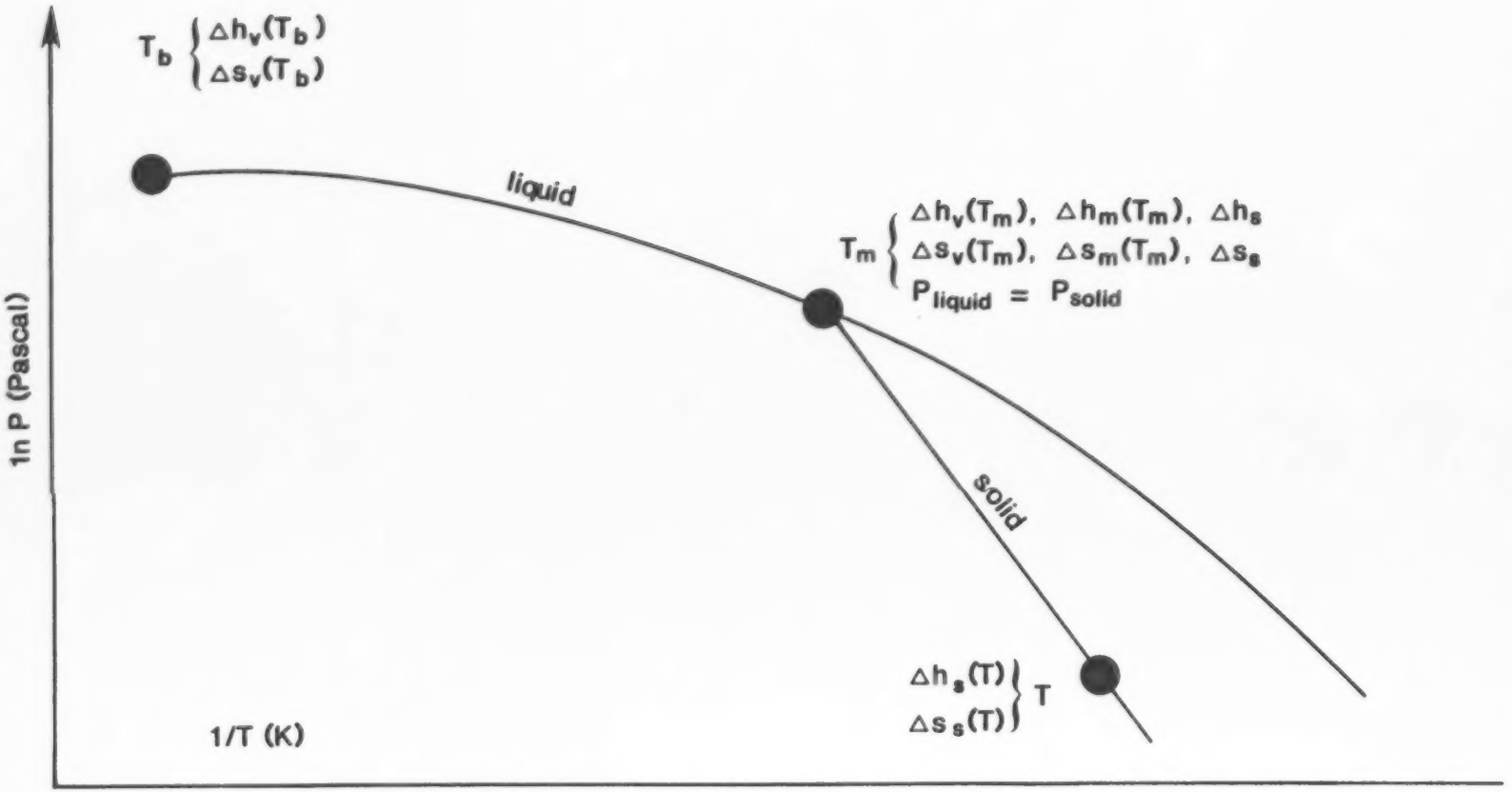

T_b { $\Delta h_v(T_b)$ $\Delta s_v(T_b)$
liquid
T_m { $\Delta h_v(T_m)$, $\Delta h_m(T_m)$, Δh_s $\Delta s_v(T_m)$, $\Delta s_m(T_m)$, Δs_s $P_{liquid} = P_{solid}$
solid
$\Delta h_s(T)$ $\Delta s_s(T)$ } T
ln P (Pascal)
1/T (K)

Figure 1. Relationship Between the Vapor Pressures of the Solid and Liquid Phases at Temperatures T, the Melting Point (T_m), and the Boiling Point (T_b) (Continued)

At the Boiling Point

$$\Delta h_v(T_b) = T_b K_F (36.61 + R \ln T_b) \quad (I)$$

$$\Delta s_v(T_b) = \Delta h_v(T_b) / T_b + R \ln P^o \quad (II)$$

In the Liquid Phase

$$\Delta h_v(T_2) = \Delta h_v(T_1) + \int_{T_1}^{T_2} \Delta c_p^{gas\text{-}liq.} dT \quad (III)$$

gives after integration for $T_1 = T_b$ and $T_2 = T$:

$$\Delta h_v(T) = \Delta h_v(T_b) (1 + K(1 - T/T_b)) \quad (IV)$$

with $K = - T_b \Delta c_p^{gas\text{-}liq.} / h_v(T_b)$ (V)

h - molar enthalpy
s - molar entropy
q - molar gibbs free energy
c_p - molar heat capacity

T_b - boiling point (K)
T_m - melting point (K)
R - 8.314 J/mol K
P(T) - vapor pressure at T(K)
Subscript$_s$: sublimation
Subscript$_v$: vaporization
Subscript$_m$: fusion

Setting (IV) into the Clausius-Clapeyron equation,

$$\int_P^{P^o} d \ln P(T) = \int_T^{T_b} \Delta h_v(T_b) (1 + K(1 - T/T_b)) / R T^2 \, dT \quad (VI)$$

gives after integration from the melting to the boiling point:

$$\ln P(T_m) = \ln P^o - (\Delta h_v(T_b) / R T_b) ((1 + K)(T_b/T_m - 1) - K \ln (T_b/T_m)) \quad (VII)$$

At the Melting Point

From $\Delta g_s = \Delta g_m + \Delta g_v$ (VIII), and $\Delta g = \Delta h - T \Delta s$ (X) follows

$$\Delta h_m = \Delta h_s - \Delta h_v \quad (IX)$$

$$s_m = \Delta s_s - \Delta s_v \quad (XI)$$

For $T = T_m$: $\Delta g_m (T_m) = 0$ (XII) and

$$\Delta s_m(T_m) = \Delta h_m(T_m) / T_m \quad (XIII)$$

From $\Delta g_v = - R T \ln P_{liq.} = \Delta h_v - T \Delta s_v$ (XIV)

follows for $T = T_m$ $\Delta s_v(T_m) = R \ln P_{liq.}(T_m) + \Delta h_v(T_m) / T_m$ (XV)

(IV) for $T = T_m$: $\Delta h_v(T_m) = \Delta h_v(T_b) (1 + K(1 - T_m/T_b))$ (IV)

In the Solid Phase

$\Delta g_s(T) = - R T \ln P_{solid}(T) = \Delta h_s(T) - T \Delta s_s(T)$ gives: (XVI)

$$R \ln P_{solid}(T) = (\Delta s_s(T_m) + \int_{T_m}^{T} \Delta c_p^{g\text{-}s}/T \, dT) - (\Delta h_s(T_m)/T + \int_{T_m}^{T} \Delta c_p^{g\text{-}s} dT) \quad (XVII)$$

$$R \ln P_{solid}(T) = \Delta s_s(T_m) - \Delta h_s(T_m) / T \quad (XVIII)$$

enthalpies of evaporation can be estimated by equation IV for the melting points. Expression XV, which is obtained from XIV, permits the calculation of the entropy of evaporation at T_m in combination with IV and VII.

Enthalpies and entropies of fusion can be predicted for T_m from experimental enthalpies and entropies of sublimation (at T_m) by IV, IX, XI, and XV. A correlation of the evaluated enthalpies of fusion with the degree of chlorine substitution enable the estimation of enthalpies and entropies by XIII of fusion for n-chlorinated dioxins. Equations IX and XI allow the conversion of predicted enthalpies and entropies of evaporation to enthalpies and entropies of sublimation. Solid state vapor pressure curves can now be predicted by equation XVII which is obtained from XVI.

The differences of the heat capacities of the gas and the solid phases equal the rotational and the translational heat capacities of the gases minus the lattice-mode heat capacities:

$$c_p^{\text{gas-solid}} = 4R - c_{\text{lattice}}$$

The lattice parts can be estimated by the rule of Dulong and Petit approaching 6R at ambient temperatures for crystals composed of molecules with three nonzero moments of inertia. Solid to gas heat capacity changes of -16.6 J/mol K were therefore assumed except for anthracene (-31.4 J/mol K) and 3,6-DiCDF (-45 J/mol K). The latter values were determined from the strongly bent sublimation curves of the two compounds. Equation XVII can be approximated by XVIII to calculate vapor pressures over a narrow temperature range.

The boiling point (T_b) appears in several expressions and was determined in an iterative procedure: enthalpies and entropies of sublimation were determined by linear regressions of the experimental vapor pressure data over the indicated temperature intervals (Table 49). They hold for the mid-temperatures of the investigated temperature ranges defined by:

$$T_{mid} = 2\ (T_{max} - T_{min})/(T_{max} + T_{min})$$

The temperature ranges were recalculated for the melting points by means of the bracket expressions of equation XVII. These equations were entered along with I, II, IV, V, VII, IX, XI, XIII, XV, and XVII into the spreadsheet. The boiling points were then set for correct prediction of the vapor pressures at the melting points, given by:

$$P_{liquid}(T_m) = P_{solid}(T_m)$$

Rordorf's estimates on the heat capacity and the boiling point of chlorinated dioxins and furans and the extrapolated and estimated values for other thermal properties are shown in Table 49.

Both the PCDFs and PCDDs exhibit the same tendency of strongly decreasing vapor pressure with increasing chlorine substitution. Correspondingly, the boiling point temperature also increases with the number of chlorine atoms. With the boiling point temperature for tri-CDD and tri-CDF and higher chlorinated PCDDs and PCDFs ranging between 375°C and 537°C, a first approximation of the thermodynamic conditions would favor the formation of tri- and higher chlorinated PCDFs and PCDDs in PCB transformer fire incidents. This estimation of the thermodynamics of a PCB transformer fire appears to be supported by the analysis of products generated at the incident site as well as in laboratory pyrolysis and combustion studies.

PCDF AND PCDD LEVELS IN PCB TRANSFORMERS UNDER NORMAL USE CONDITIONS

An early concern was whether PCDFs and PCDDs are formed in PCB transformers under normal use conditions. EPRI conducted a round-robin study with three participating laboratories using four samples of dielectric fluids taken from in-service transformer and capacitor units.[8] The average total congener class concentration found for PCDFs is shown in Table 50.[43] Furthermore, EPA obtained fluid samples from transformers that were involved in fire incidents at Miami, FL, Binghamton, NY, and Chicago, IL.[4] Total PCDFs (Table 51) in the used fluids is within the range of PCDF values previously reported for stock material (Table 52). It does not appear that, under normal use conditions, PCDFs are generated to any significant extent in the transformer.[45]

Table 49. Vapor Pressure Correlations of Dibenzodioxins, Dibenzofurans, Xanthenes, and Anthracenes[42]

	h_s (J/mol) obs.	s_s (J/mol K) obs.	meas. range (°C) obs.	t_m (°C) obs.	$\ln P(T_m)$ (Pa) extr.	$c_p(g-1)$ (J/mol K) est.	K	$s_v(T_b)$ (J/mol K)	$s_v(T_m)$	$h_v(T_m)$ (kJ/mol)	$s_m(T_m)$ (J/mol K)	$h_m(T_m)$ (kJ/mol) pred.	$h_m(T_m)$ (kJ/mol) obs.	T_b (°C) pred.	T_b (°C) obs.
DD[a]	92250	285.29	30-60	122.5[1]	6.22	-113.3	1.26	185.9	228	68.4	57	22.6	23.2[2]	283.5	266[2]
1-MCDD	98550	293.8	30-65	105[1]	3.97	-108.9	1.20	186.4	237	76.2	56	21.4	23.2[2]	315.5	296[2]
2-MCDD	97160	292.1	32-75	89[1]	2.85	-108.9	1.20	186.4	241	78.1	51	18.5	23.1[2]	316.0	298[2]
2,3-DCDD	106230	291.08	33-101	163.5[1]	5.69	-104.5	1.15	186.9	230	77.8	61	26.7		358.0	
2,7-DCDD	105510	279.05	41-101	209.5[1]	7.16	-104.5	1.14	187.2	224	76.4	55	26.8		374.5	
2,8-DCDD	109010	291.87	32-90	151[1]	4.14	-104.5	1.14	187.3	237	84.1	55	23.3		382.5	
1,3,7-TCDD	116200	304.77	37-100	148.5[1]	3.47	-100.0	1.09	187.5	237	86.4	67	28.4	30.8[2]	398.0	
1,2,4-TCDD	118790	322.16	37-101	128.5[1]	3.15	-100.0	1.09	187.2	238	83.9	84	33.9		375.0	
1,2,3,4-TCDD	118530	298.15	60-120	189[1]	4.96	-95.6	1.04	187.7	231	85.6	68	31.2		419.0	
2,3,7,8-TCDD	124001[8]	287.6[8]	30-71[8]	305[1]	8.51	-95.6	1.04	188.1	219	79.9	69	39.9	38.97[7]	446.5	
OCDD	151130	316.48	111-201	331[1]	7.87	-77.9	0.84	188.8	215	86.7	102	61.4		510.0	

[a]The table displays observed (obs.), extrapolated (extr.), estimated (est.), and predicted values (pred. or no indication).

[1]A.E. Pohland and G.C. Yang, J. Agr. Food Chem. 20:1093-1099 (1972).

[2]B.F. Rordorf, B. Nickler, and A. Geoffroy, unpublished results.

[3]CRC Handbook of Data on Organic Compounds, CRC Press, Boca Raton, FL (1980).

[4]J. Dazzi, R. Kirchmayr, and D. Henri, Swiss Patent Appl. 4028/73, Ger.Offen. 2:411,655 (1974).

[5]R. Goethe and C.A. Wachtmeister, Acta. Chem. Scand. 26:2523 (1972).

[6]P. Goursot, H.L. Girdhar, and E.F. Westrum, Jr., J. Phys. Chem. 74:2538-2541 (1970).

[7]F.P. Boer, F.P. van Remoortere, and W.W. Huelder, J. Amer. Chem. Soc. 94:1006-1007 (1972).

[8]J.M. Schroy, F.D. Hileman, and S.C. Cheng, Chemosphere 14:873-876 (1985).

[9]9,10-Dihydroanthracene.

Estimated from chlorine correlation on dioxin data:

[10]$h_m(T_m) = 13.61 + 5.75 * X \pm 2$ kJ/mol

[11]$T_b(K) = 283 + 42.0 * X - 1.73 * X * X \pm 15$ (X = chlorine subst. #).

Table 49. Vapor Pressure Correlations of Dibenzodioxins, Dibenzofurans, Xanthenes, and Anthracenes (Continued)

	h_s (J/mol) obs.	s_s (J/mol K) obs.	meas. range (°C) obs.	t_m (°C) obs.	$\ln P(T_m)$ (Pa) extr.	$c_p^{(g-l)}$ (J/mol K) est.	K	$s_v(T_b)$ (J/mol K)	$s_v(T_m)$	$h_v(T_m)$ (kJ/mol)	$s_m(T_m)$ (J/mol K)	$h_m(T_m)$ (kJ/mol) pred.	$h_m(T_m)$ (kJ/mol) obs.	T_b (°C) pred.	T_b (°C) obs.
DF[a]	85630	278.49	31-70	86.5[3]	4.85	-87.6	0.97	185.7	224	65.4	54	19.6		273.0	287[3]
3,6-DCDF	110870	300.9	32-101	188.0[2]	7.03	-78.7	0.86	186.9	226	70.7	75	34.5	32.4[2]	357	
2,4,8-TCDF	112300	299.31	45-150	154[4]	4.35	-74.3	0.81	187.4	223	78.7	76	32.6		392.5	375[2]
OCDF	149430	323.07	100-201	259[4]	5.03	-52.1	0.56	189.0	215	90.0	108	57.5		537.0	
Xanthene	92450	284.79	32-80	100.5[3]	4.48	-121.9	1.35	186.0	239	74.5	46	17.1		293.0	311[3]
1,2,4,5,7,8-HCX	147000	331.32	80-176	261.5[5]	6.70	-95.4	1.03	188.2	224	87.2	107	57.4		463.0	
Anthracene	98745	274.38	45-100	215.8[6]	8.50	-79.0	0.87	186.7	216	65.5	59	28.6	29.4[6]	340.0	340[3]
DH-Anthr.[9]	93221	284.96	31-96	111[3]	5.07	-130.5	1.45	186.0	239	74.8	46	17.6		293.0	305[3]
	pred.	pred.	calc.		pred.										
2,3,7,8-TCDD	121170	284.329	30-70	305[1]	8.71	-95.6	1.04	188.0	208	78.3	67	38.6[10]	38.9[7]	438.3[11]	

[a]The table displays observed (obs.), extrapolated (extr.), estimated (est.), and predicted values (pred. or no indication).

[1]A.E. Pohland and G.C. Yang, J. Agr. Food Chem. 20:1093-1099 (1972).
[2]B.F. Rordorf, B. Nickler, and A. Geoffroy, unpublished results.
[3]CRC Handbook of Data on Organic Compounds, CRC Press, Boca Raton, FL (1980).
[4]J. Dazzi, R. Kirchmayr, and D. Henri, Swiss Patent Appl. 4028/73, Ger.Offen. 2:411,655 (1974).
[5]R. Goethe and C.A. Wachtmeister, Acta. Chem. Scand. 26:2523 (1972).
[6]P. Goursot, H.L. Girdhar, and E.F. Westrum, Jr., J. Phys. Chem. 74:2538-2541 (1970).
[7]F.P. Boer, F.P. van Remoortere, and W.W. Huelder, J. Amer. Chem. Soc. 94:1006-1007 (1972).
[8]J.M. Schroy, F.D. Hileman, and S.C. Cheng, Chemosphere 14:873-876 (1985).

[9]9,10-Dihydroanthracene.

Estimated from chlorine correlation on dioxin data:

[10]$h_m(T_m) = 13.61 + 5.75 * X \pm 2$ kJ/mol
[11]$T_b(K) = 283 + 42.0 * X - 1.73 * X * X \pm 15$ (X = chlorine subst. #).

Table 50. Average Total Congener Class Concentrations of PCDFs in Four In-Service Dielectric Fluids[43]

CONGENER CLASS	IN-SERVICE SAMPLE (ppm)			
	ISL4A[a]	ISL3A[b]	ISL2A[c]	ISLIO[d]
TCDFs	0.1	0.5	N.D.[e]	N.D.
PeCDFs	2.6	1.6	0.01	N.D.
HxCDFs	7.6	1.6	0.01	N.D.
HpCDFs	16.3	2.0	N.D.	N.D.
OCDF	9.8	1.0	N.D.	N.D.
Total PCDFs	36.4	6.7	0.02	N.D.

[a]ISL4A = Askarel fluid with 70% Aroclor 1260/30% trichlorobenzene from transformer after 31 years of service.

[b]ISL3A = As above, except 20 years of service; contained 0.5-2.0 mcg/g PCDF.

[c]ISL2A = Askarel containing Aroclor 1242 from capacitor that had bulged but not ruptured.

[d]ISLIO = Mineral oil contaminated with 100 mcg/g PCB from transformer that had failed in service by arcing.

[e]N.D. = Not Detected.

Table 51. Analysis of Fluids Involved in Transformer Fire Incidents[44]

	MIAMI, FL[1] (May 29, 1984) (mcg/g)	BINGHAMTON, NY[2] (February 5, 1981) (mcg/g)	CHICAGO, IL[3] (September 28, 1981) (mcg/g)
PCDDs	N.D.[a]	N.D.[a]	N.D.[a]
PCDFs (Total)	6.0	16.2	3.0
Tetra-CDFs	0.31	0.48	<0.01
Penta-CDFs	0.78	1.1	0.053
Hexa-CDFs	2.2	11.0	0.47
Hepta-CDFs	1.3	3.2	1.4
Octa-CDF	1.4	0.41	1.1
Chlorobenzenes (Total)	430,000	350,000	160,000
Trichlorobenzenes	260,000[b]	230,000[b]	100,000[b]
Tetrachlorobenzenes	140,000[b]	110,000[b]	51,000[b]
Pentachlorobenzene	29,000[b]	13,000[b]	5,500[b]
Hexachlorobenzene	900[d]	45[d]	64[b]
PCBs (Total)	410,000	580,000	110,000
Monochlorobiphenyls	320[c]	230[c]	<100[c]
Dichlorobiphenyls	1,100[c]	730[c]	<150
Trichlorobiphenyls	2,600[c]	3,500[d]	<200
Tetrachlorobiphenyls	2,000[c]	88,000	<400
Pentachlorobiphenyls	31,000[c]	300,000	11,000
Hexachlorobiphenyls	160,000[c]	160,000[d]	49,000[c]
Heptachlorobiphenyls	170,000[c]	24,000	45,000
Octachlorobiphenyls	32,000[c]	<800	7,300
Nonachlorobiphenyls	14,000	<1,200	<1,600
Decachlorobiphenyl	<2,800[c]	<3,500	<4,700

[a] Detection limits approximately 0.01 mcg/g for PCDFs/PCDDs.
[b] Results of analysis at a dilution of 0.1 mg of oil/ml of hexane.
[c] Results of analysis at a dilution of 2.5 mg of oil/ml of hexane.
[d] Results of analysis at a dilution of 0.25 mg of oil/ml of hexane.

[1] Askarel Type A: 60% PCBs with 60% chlorine (Aroclor 1260) with 40% trichlorobenzenes mixture.
[2] Askarel Type D: 70% PCBs containing 54% chlorine (Aroclor 1254) and 30% trichlorobenzenes mixture.
[3] Mineral Oil with 25% PCBs (Aroclor 1260).

ELECTRICAL ARCING AND PCDD AND PCDF LEVELS

Electrical arcing has been implicated as one of the causes of PCB transformer and capacitor fires, raising concerns as to whether arcing causes the formation of PCDDs and PCDFs in the transformer fluid. As discussed earlier, Rouse *et al.*, conducted several experiments involving the arcing of electrical energy through fluids containing various formulations of transformer fluids.[34] The results of this study were presented in Section 4, Tables 30 and 31. The data show no difference in the PCDF level before and after electrical arcings. The authors suggest that the level of oxygen is very low in the transformer (although it can occur in the cardboard components) and thus does not offer the environment for combustion and the formation of PCDFs and PCDDs.

Dellinger *et al.*, has conducted studies to determine the effect of temperature and oxygen concentration on the rate of formation and destruction of PCDFs as well as the thermal stability of the parent PCB.[46] The thermal degradation of a single PCB isomer was conducted under four reaction atmospheres at a constant gas phase residence time of 2.0 seconds. The isomer selected for study was 2,4,5,3',4'-pentachlorobiphenyl (2,4,5,3',4'-PeCB). The oxygen availability in the reaction atmosphere is described using the equivalence ratio, phi (ϕ). Phi is defined as the ratio of fuel to oxygen actually in the reactor divided by the ratio of fuel to oxygen required for complete combustion. The values of phi used in this study were 3.0, 1.0, 0.2, and 0.05, which range from oxygen-starved to very oxygen-rich conditions as the values of phi become progressively smaller. A phi of 1.0 means there is exactly enough oxygen available for complete combustion; thus, the percent excess oxygen is zero. Thermal degradation experiments were conducted at various temperatures ranging from 500-1000°C. The results are shown in Table 53 and Figures 2 and 3.

This study shows that the yields of PCDFs formed from the thermal degradation of 2,4,5,3',4'-PeCB are on the order of 1 to 2 percent; and these yields increase as the oxygen concentration increases (ϕ = 3.0 to ϕ = 0.05). The predominant mechanism for their formation is HCl elimination.

Table 52. Levels of PCDFs in Commercial PCBs[14]

SAMPLE	PCDF LEVEL (ppm)					
	TRI-	TETRA-	PENTA-	HEXA-	HEPTA-	TOTAL
Aroclor 1254	0.10	0.25	0.70	0.81	N.D.[a]	1.9
Aroclor 1254 (lot KK602)	---	0.05	0.10	0.02	N.D.	0.2
Aroclor 1260	0.06	0.30	1.00	1.10	1.35	3.8
Clorphen T64	0.10	0.30	1.73	2.45	0.82	5.4
Prodelec 3010	0.41	1.08	0.35	0.07	N.D.	2.0
Mitsubishi (used)	2.13	4.00	3.30	0.53	N.D.	10.0

[a]N.D. = Not Detected.

Table 53. Maximum Weight Percentage Yield of PCDFs as a Function of Reaction Atmosphere[46]

ϕ	TEMPERATURE OF MAXIMUM YIELD (°C)	WEIGHT % YIELD			
		TRI-CDFs	TETRA-CDFs	PENTA-CDFs	TOTAL PCDFs
0.05	750	0.66	4.3	2.0	6.9
0.2	800	0.34	1.7	0.56	2.6
1.0	850	0.13	1.3	0.25	1.7
3.0	900	0.068	0.71	0.21	0.99

Figure 2. Weight Percentage Yield of PCDFs as a Function of Oxygen Concentration[46]

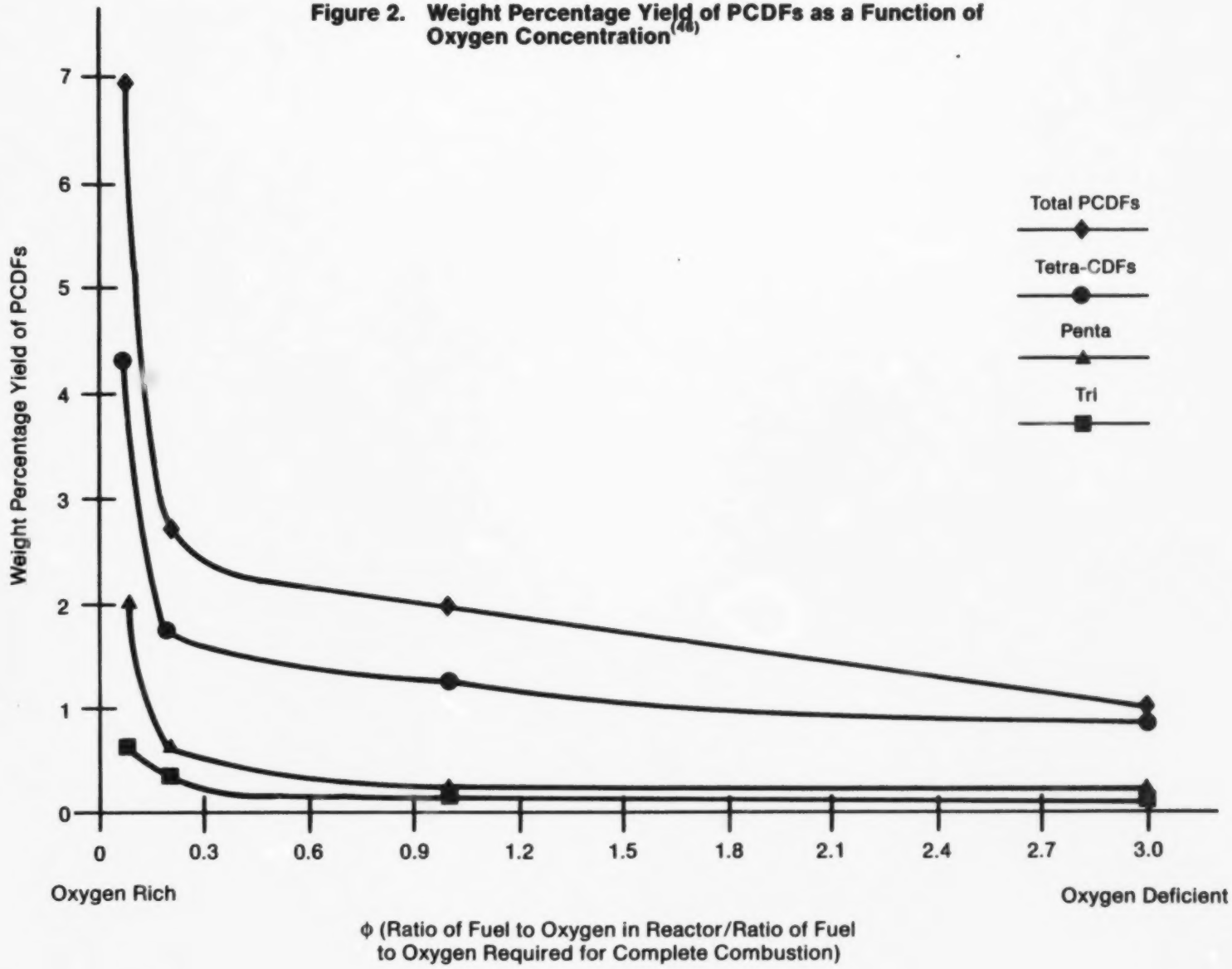
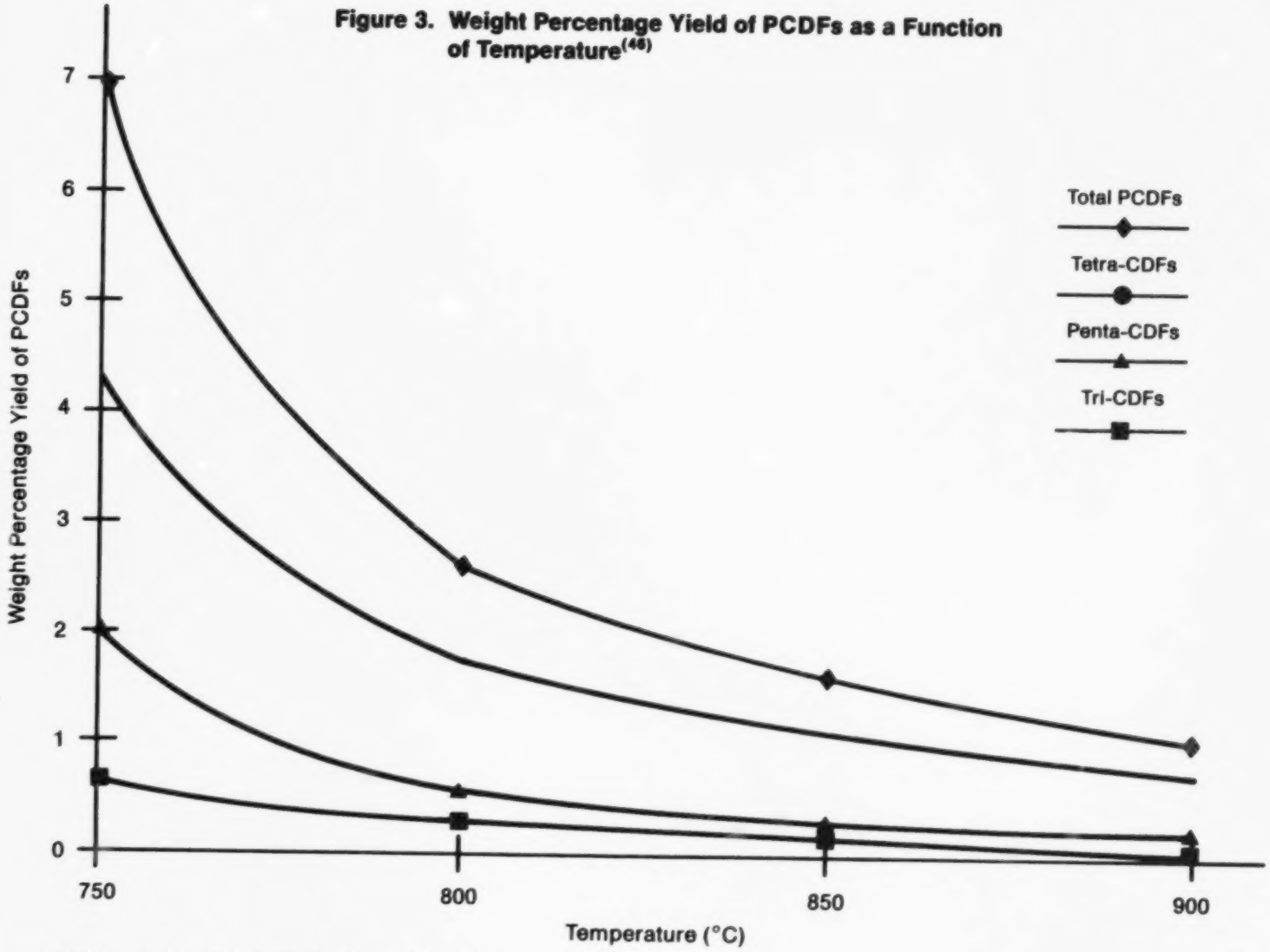


Figure 3. Weight Percentage Yield of PCDFs as a Function of Temperature[46]



Fluid = 2, 4, 5, 3′, 4′- Pentachlorobiphenyl

CORRELATION OF COMBUSTION/PYROLYSIS PRODUCTS GENERATED AND CONSTITUENTS OF TRANSFORMER FLUIDS

Another issue of interest is the correlation between the contaminants found in the soot and the transformer fluid. The ability to predict the type and the quantity of toxic contaminants that may form in a PCB transformer/capacitor fire is of prime importance in the development of prevention and control measures. Because of the scarcity and generally poor quality of data obtained from PCB transformer fire incidents, pyrolytic studies under laboratory-controlled conditions have been employed.

EPA, through a contract with Midwest Research Institute, Kansas City, MO, has conducted a study to evaluate thermal degradation products using a bench scale thermal destruction system.(7) Details of this study were presented in Section 4 of this report. The results indicate that both temperature and oxygen significantly affect PCDF yield. Statistical analysis showed a linear relationship for PCDFs formed versus the concentration of PCBs. Figures 4 and 5 represent the relationship between the amount of PCDFs formed and the concentration of PCBs in the fluid.

In a study reported by Gervason, askarel fluid mixtures of 60% PCBs and 40% trichlorobenzenes were combusted under varying flame temperatures.(33) The results of this study were presented in Tables 29 and 41. Figures 6 and 7, depicting these results graphically, indicate that the optimal temperature for the formation of PCDFs and PCDDs is approximately 600°C. This finding is in fair agreement with the work done at the Midwest Research Institute, where the optimal temperature for PCDF formation from pyrolysis of PCBs was approximately 675°C (Figure 8).(7)

Under optimal conditions, PCDFs are formed from mineral oil or silicone oil contaminated with PCBs at $\geq$ 5 ppm. PCDFs were also formed from a trichlorobenzene dielectric fluid that contained no detectable PCBs. These results supported earlier laboratory work and analytical results of soot material from transformer and capacitor fires, which determined that chlorobenzenes are required for PCDD formation.

Figure 4. Concentration of PCDFs Formed as a Function of PCB Concentration [7]

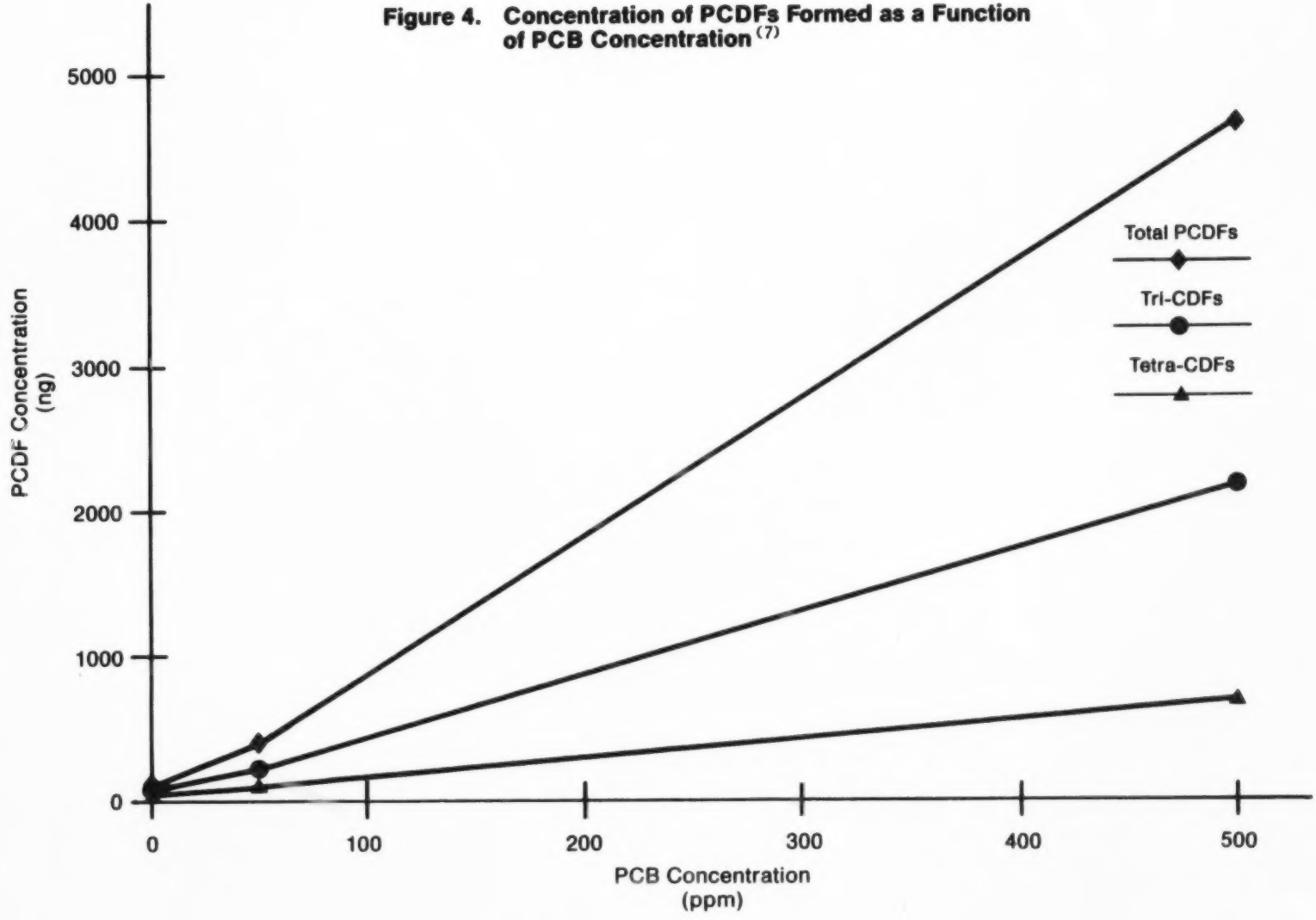


Figure 5. Concentration of PCDFs Formed in PCB-Spiked Mineral Oil [7]

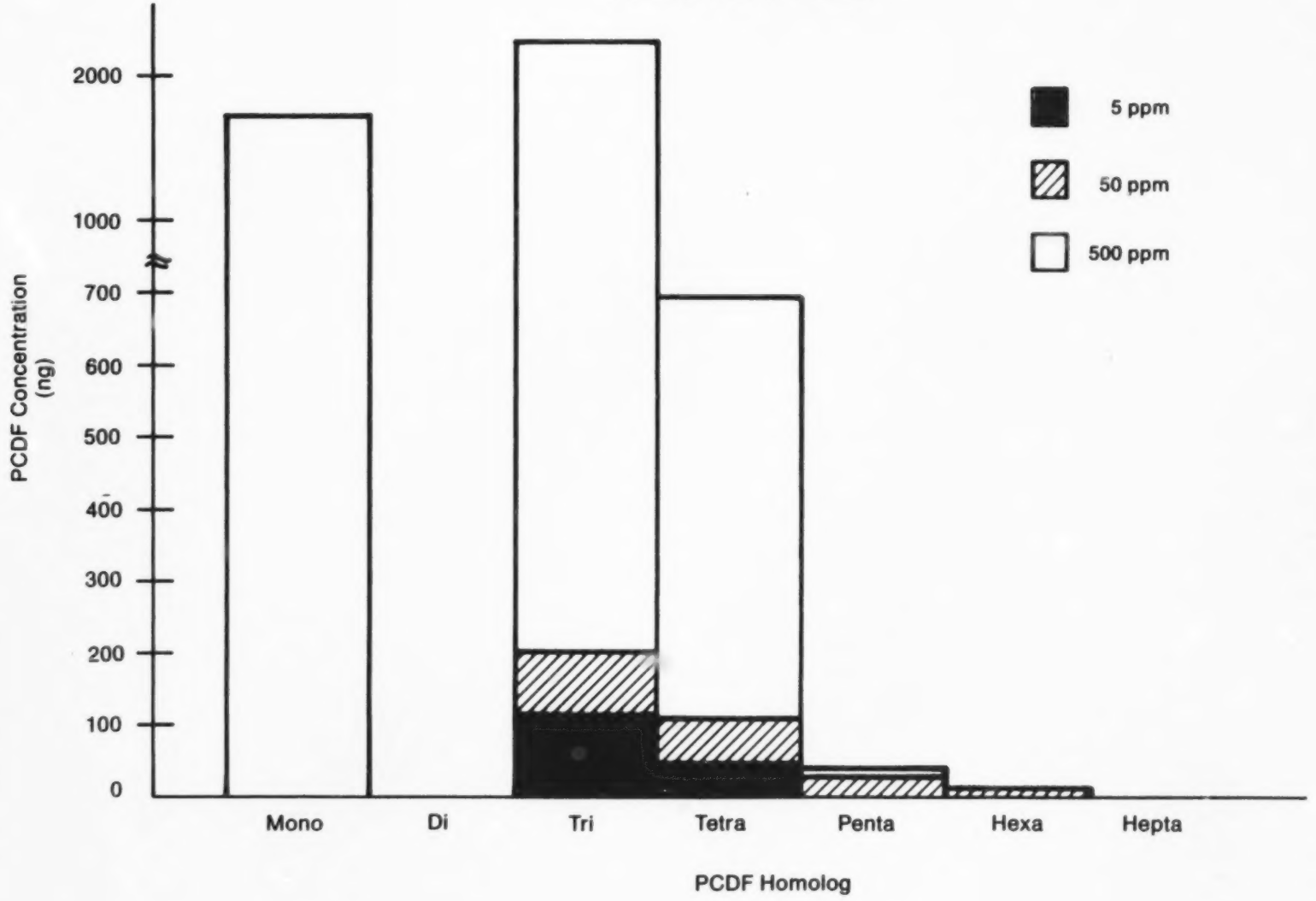


Figure 6. Concentration of PCDFs Formed as a Function of Temperature[33]

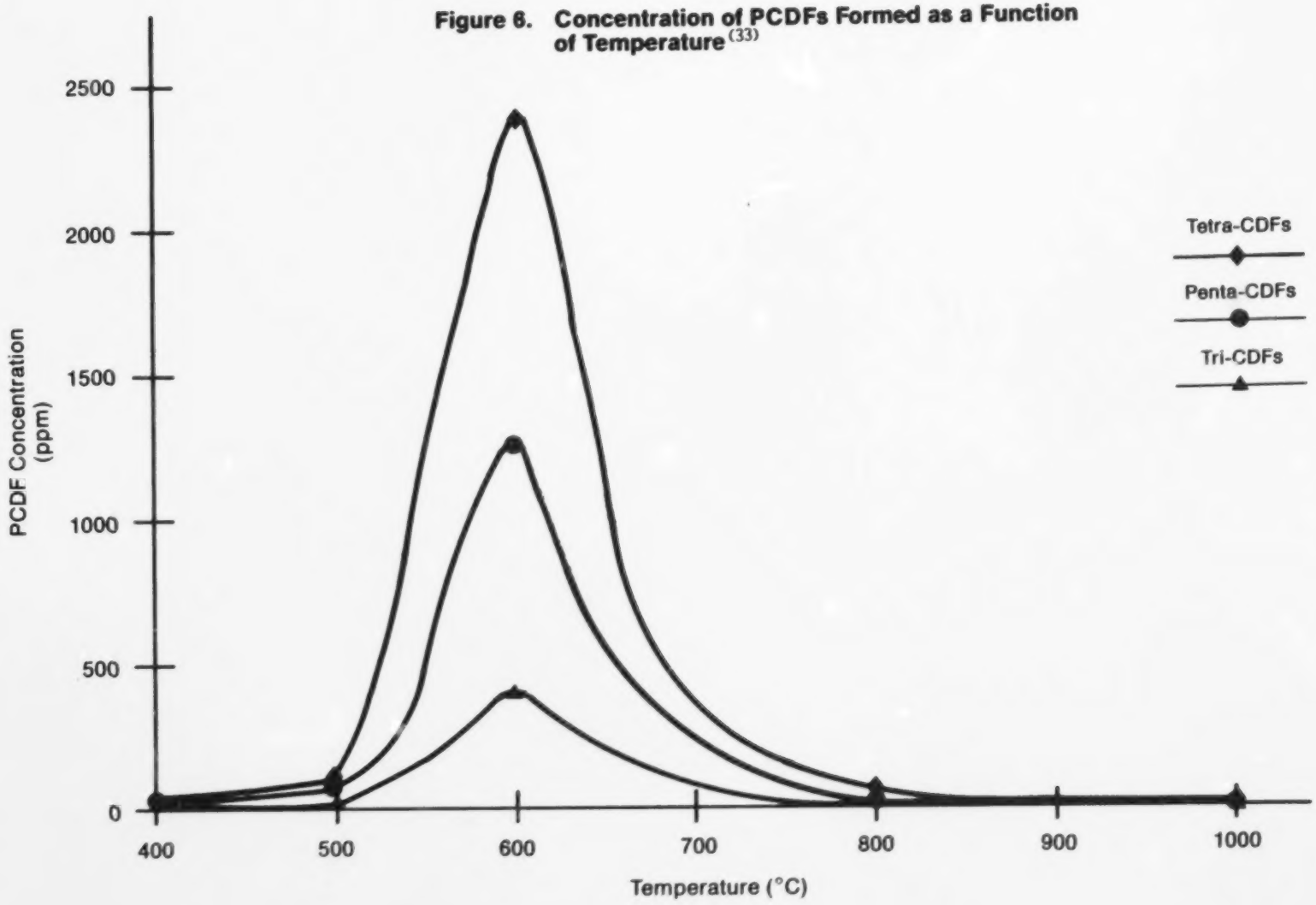


Figure 7. Concentration of TCDD Formed as a Function of Temperature[33]

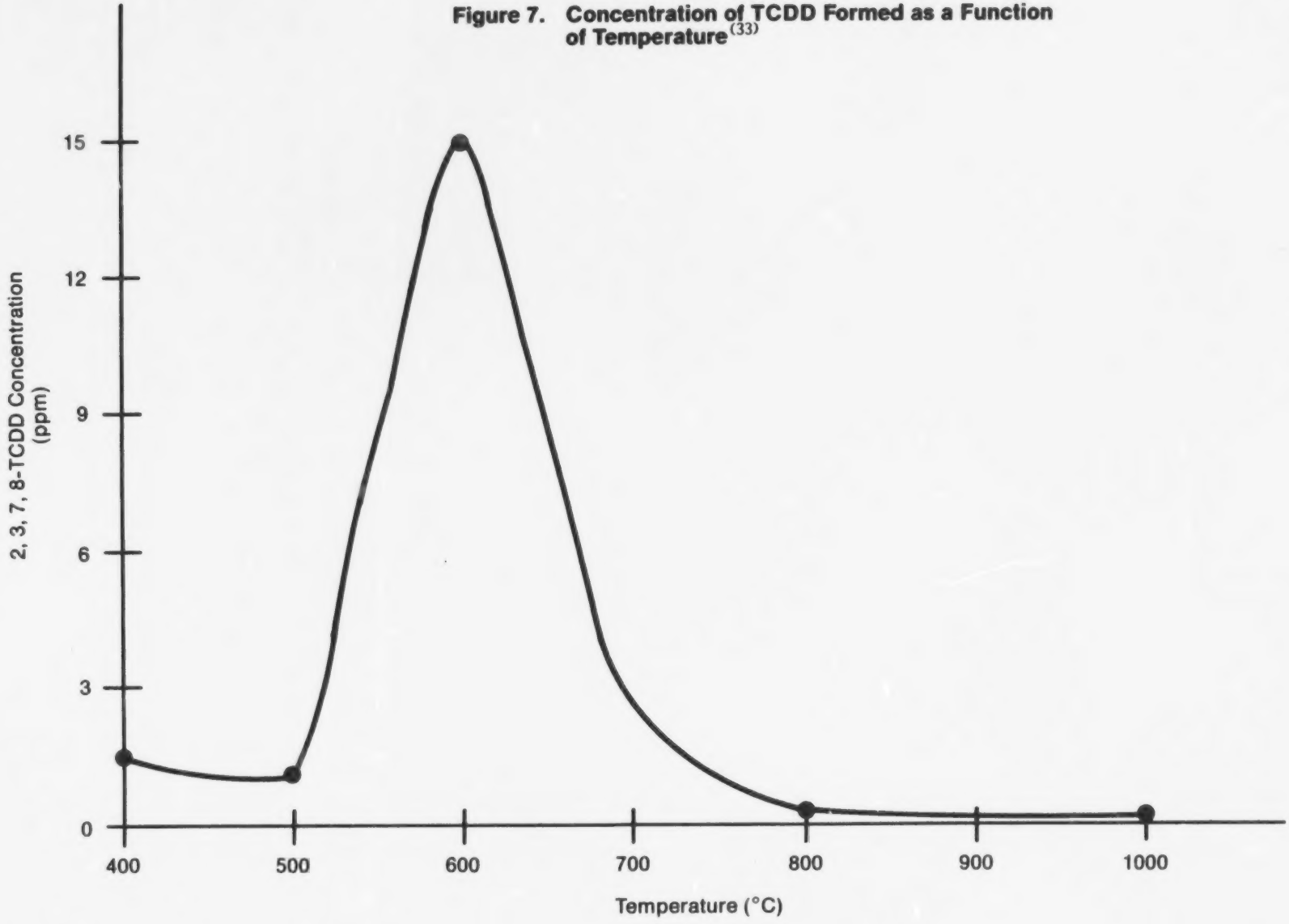
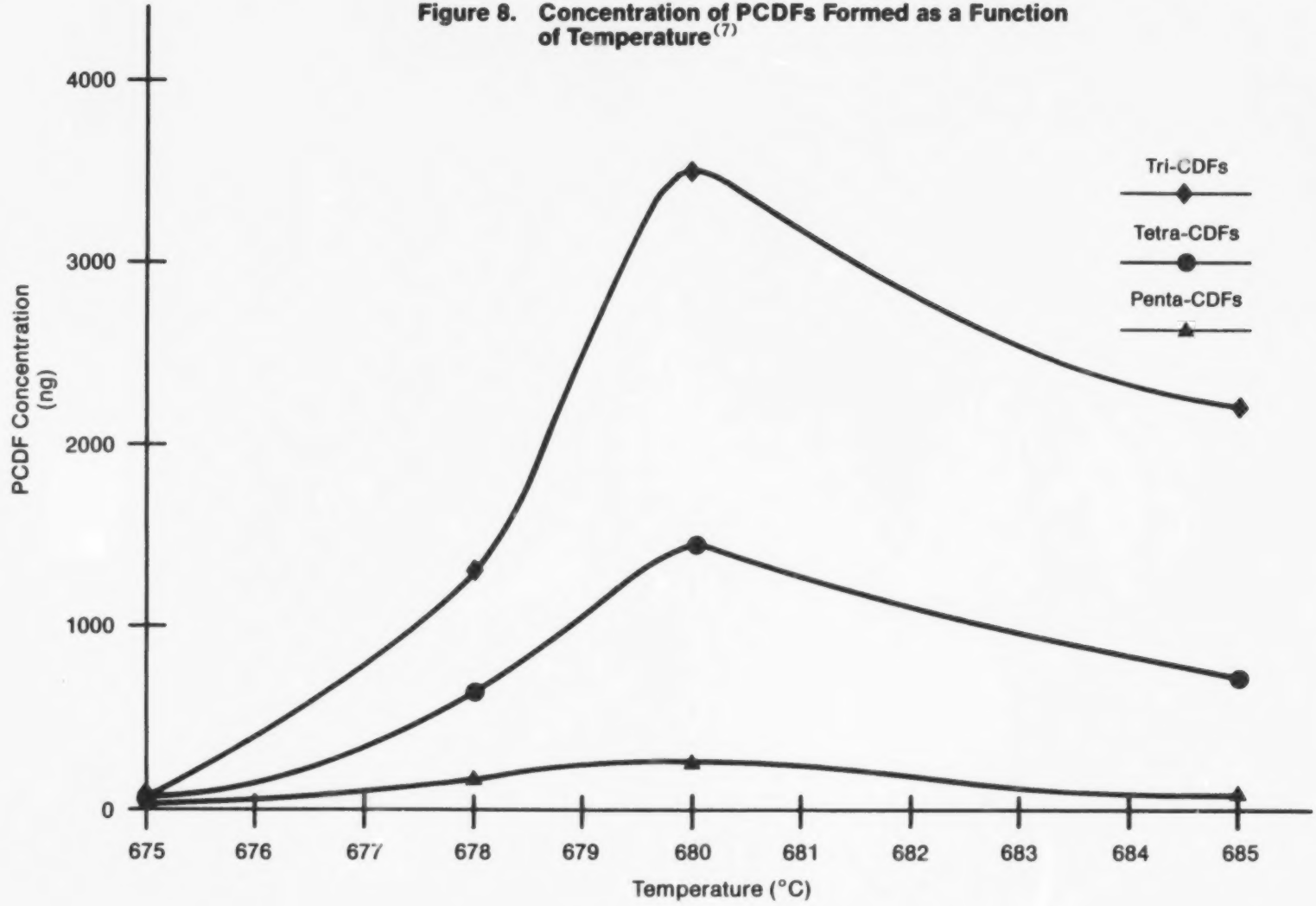


Figure 8. Concentration of PCDFs Formed as a Function of Temperature[7]



EPRI has also supported a major study of the thermal conversion of various transformer fluid formulations to PCDFs and PCDDs.[8,43] Fluids that have been studied include mineral oil, tetrachloroethylene (TCE), and silicone oil, all spiked with Aroclor 1254. 100 mcl samples were either pyrolyzed (heated in an oxygen-deficient environment) or combusted (injected into a flame or heated under conditions resulting in self-ignition). Pyrolyses were conducted using a simple thermostatically controlled apparatus, capable of accommodating glass or quartz tubes of diameters up to 6 cm within its 9-cm-long heated region. To simulate more accurately certain catastrophic incidents, pyrolyses were conducted at atmospheric pressure.

Tables 54 and 55, and Figures 9, 10, and 11 summarize the results of the EPRI study. All data are consistent with the proposition that tetra- and penta-CDF yields are roughly proportional to PCB concentrations in the starting material. An interesting feature of the mineral oil/Aroclor 1254 data is the clear and reproducible differences between the patterns of tetra-CDFs and penta-CDFs formed by pyrolysis of neat Aroclor 1254 versus those formed by pyrolysis of the 5,000-ppm mixture. For example, 2,3,7,8-TCDF and co-eluters comprise 16-21% of the tetra-CDF mixture formed from neat Aroclor, but they comprise 45-55% of the mixture from mineral oil/Aroclor. Furthermore, combustion of biphenyl in TCE produced decreasing net dibenzofuran as the residence time was varied from 18 seconds to 6 seconds and the wall temperature maintained at 450°C. In contrast, at 550°C, there is a net increase in dibenzofuran yield as residence time decreases. This suggests that at the higher temperature, significant dibenzofuran destruction is occurring. There are also large effects on dibenzofuran yield in the presence of different solvents. Typically, yields obtained with combustion in TCE are much higher than those obtained in silicone or mineral oil. Some sharp differences on the effects of particular variable parameters on dibenzofuran yields have also been noted.

Both EPA's and EPRI's pyrolytic and combustion studies support the proposition that the amount and the specific PCDF isomers found are related to the concentration of and the PCB homologs in the transformer fluid. Additional supporting data include EPA's data on the transformer oil and the generated

Table 54. Amount of PCDFs Formed from Pyrolysis of Aroclor 1254[8]

PCB CONTAMINANT	TETRA	PENTA	HEXA	HEPTA
	(ng PCDF/g Aroclor 1254)			
100% 1254	6,900	13,000	6,600	60
5000 ppm PCBs in Mineral Oil	7,800	33,600	36,700	3,800
500 ppm in Mineral Oil	6,200	35,400	34,900	4,400
50 ppm in Mineral Oil	--	65,000	70,000	--
5000 ppm in Silicone	21,400	14,000	1,380	30
5000 ppm in TCE[a]	580	5,600	2,500	180

[a]TCE = Tetrachloroethylene or perchloroethylene.

Table 55. Percentage of PCDFs Formed from Combustion of Aroclor 1254[8]

PCB CONTAMINANT	TRI	TETRA	PENTA	HEXA	HEPTA
	(% PCDF/g Aroclor 1254)				
5000 ppm in Mineral Oil	0.72	0.58	0.17	--	--
500 ppm in Mineral Oil	.40	.33	.084	--	--
50 ppm in Mineral Oil	.30	.30	.056	--	--
5000 ppm in TCE[a]	.44	1.50	1.35	0.33	0.50
500 ppm in TCE	.24	.70	.661	.23	.70
50 ppm in TCE	.44	1.32	1.00	.38	.16

[a]TCE = Tetrachloroethylene or perchloroethylene.

Figure 9. Concentration of PCDFs Formed From Pyrolysis of Aroclor 1254 as a Function of PCB Concentration[8]

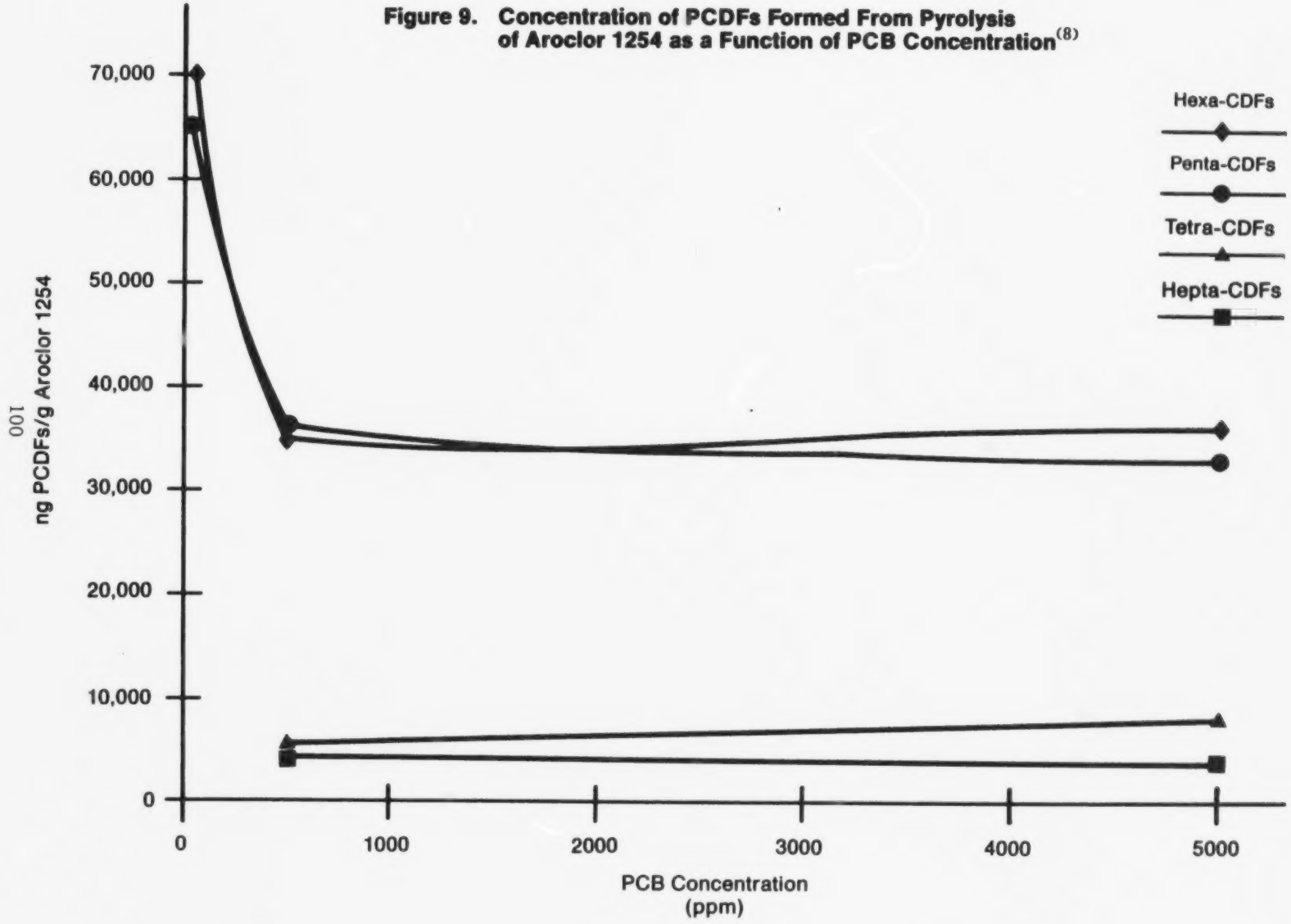


Figure 10. Percentage of PCDFs Formed from Combustion of Aroclor 1254 as a Function of PCB Concentration[8]

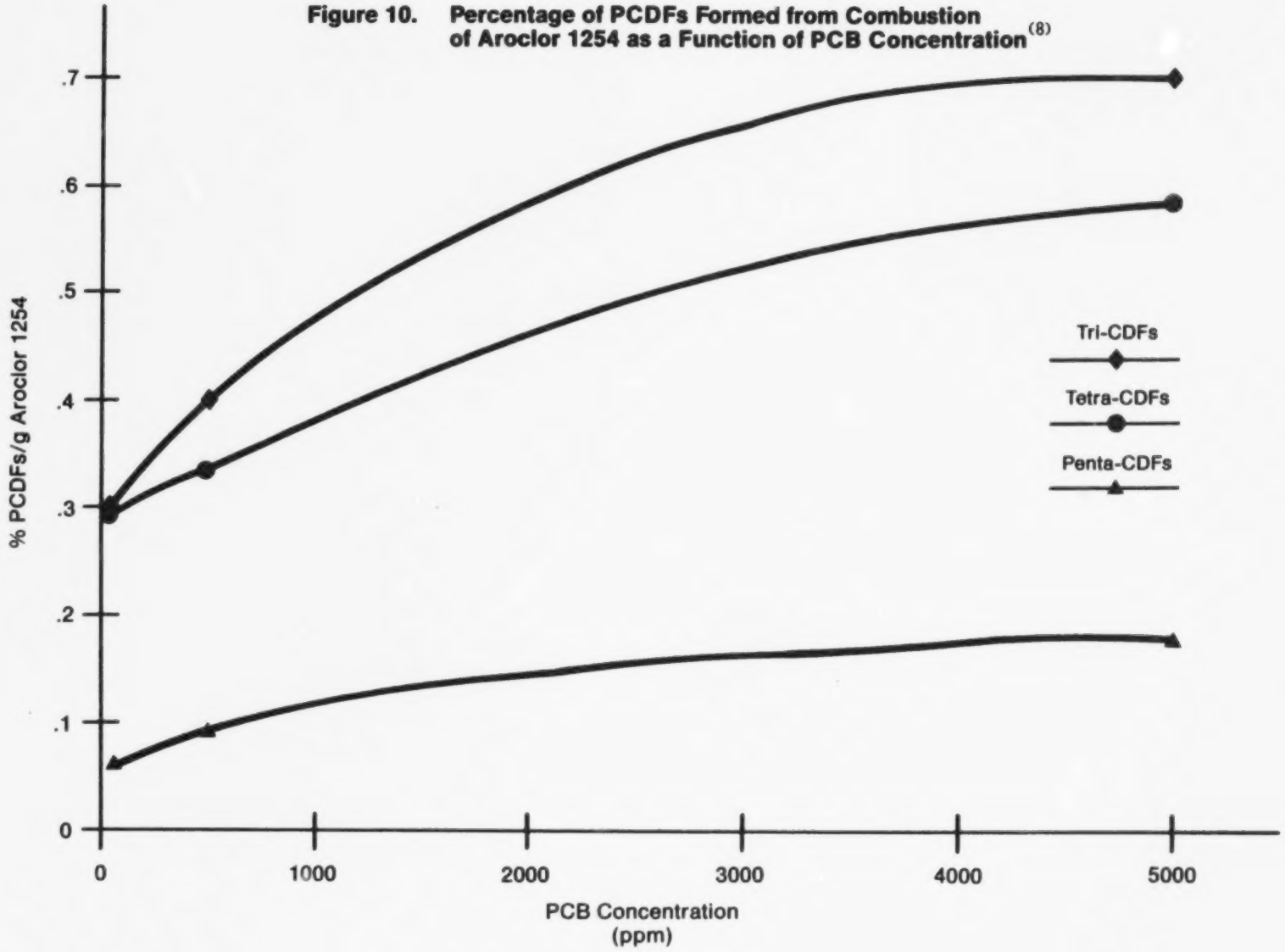
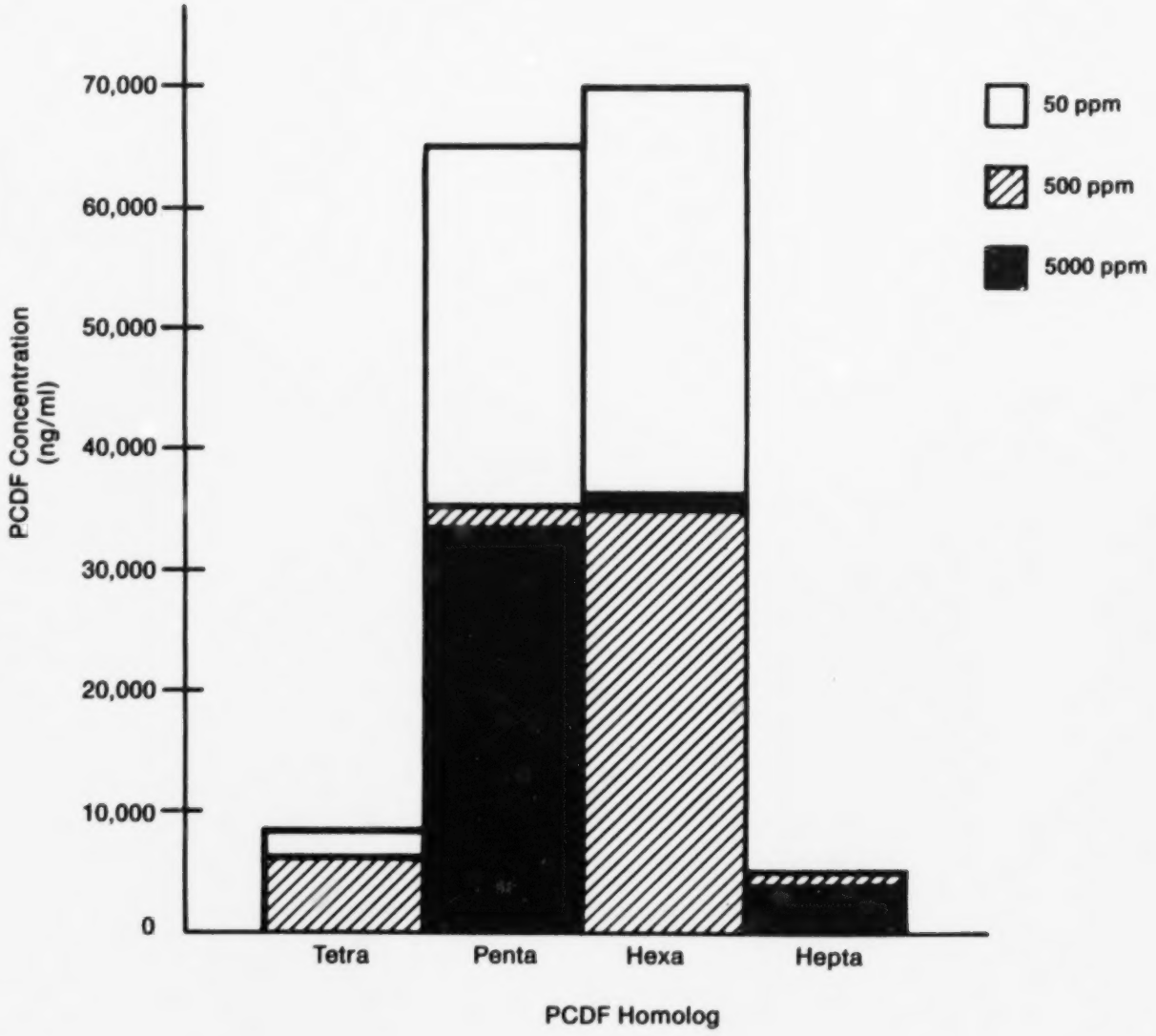


Figure 11. Concentration of PCDFs Formed in PCB-Spiked Mineral Oil by Homolog[8]



soot in the Binghamton, NY fire incident. The data on the transformer oil and soot from the Binghamton fire are presented in Table 56.

Table 56. Correlation of Analytical Data on Transformer Oil and the Generated Soot from the Binghamton, NY Incident[44]

	PCBs	PCDFs
	ISOMER/TOTAL PCBs	ISOMER/TOTAL PCDFs
Tetrachloro-	0.15	0.013
Pentachloro-	0.52	0.31
Hexachloro-	0.28	0.45
Heptachloro-	0.04	0.21
Octachloro-	0.001	0.02

Penta-CDF concentration was approximately 7% of the total PCDFs in oil. Penta-CDF concentration increased to 31% in the soot after the fire. This finding corresponds to the 52% of pentachlorobiphenyls in the transformer oil. Similar observations can be made for the hexa- and hepta-CDF concentrations in soots relative to the concentrations of hexa- and hepta-chlorinated biphenyls. The Binghamton, NY fire data also appear to indicate that the higher chlorinated biphenyls are more likely to convert to chlorinated dibenzofurans and the lower chlorinated PCBs are more likely to decompose in a transformer fire.

The finding of PCDDs in the Binghamton, NY fire incident raised concerns that PCDDs may be generated in PCB transformers. Analyses of subsequent PCB transformer fire incidents, however, identified only one other incident where PCDDs have been identified. It appears that the presence of chlorobenzene is a requirement for the formation of PCDDs, and fires involving transformers without chlorobenzenes do not generate PCDDs. The research of Erickson, Gervason, and Buser appears to support this conclusion.[7,30,33,36] Their results are shown in Figures 12, 13, 14, and 15. Figure 12 indicates that the PCDD concentration increases directly with the percentage concentration of trichlorobenzenes in fluid. Figure 13 indicates that only the trichlorobenzene fluid (with a small amount of tetra-isomer) produces significant amounts of

results are shown in Figures 12, 13, 14, and 15. Figure 12 indicates that the PCDD concentration increases directly with the percentage concentration of trichlorobenzenes in fluid. Figure 13 indicates that only the trichlorobenzene fluid (with a small amount of tetra-isomer) produces significant amounts of PCDD homologs -- the highest concentrations being the tri- and tetra-CDDs. This indicates a correlation between the lower chlorinated chlorobenzenes forming the lower chlorinated PCDDs. Figure 14 indicates that trichlorobenzenes produce mostly tetra- and penta-CDDs. This again supports the evidence that lower chlorinated chlorobenzenes form lower chlorinated PCDDs. Figure 15 indicates that trichlorobenzenes form significant amounts of tetra- and penta-CDDs, while tetrachlorobenzenes form hepta- and hexa-CDDs. The tetrachlorobenzene forms the highest concentration of hepta-CDD, and the trichlorobenzene forms the highest concentration of tetra-CDD (tri-CDD was not measured).

Figure 12. Concentration of PCDDs Formed Versus Percentage of Trichlorobenzenes in Fluid [7]

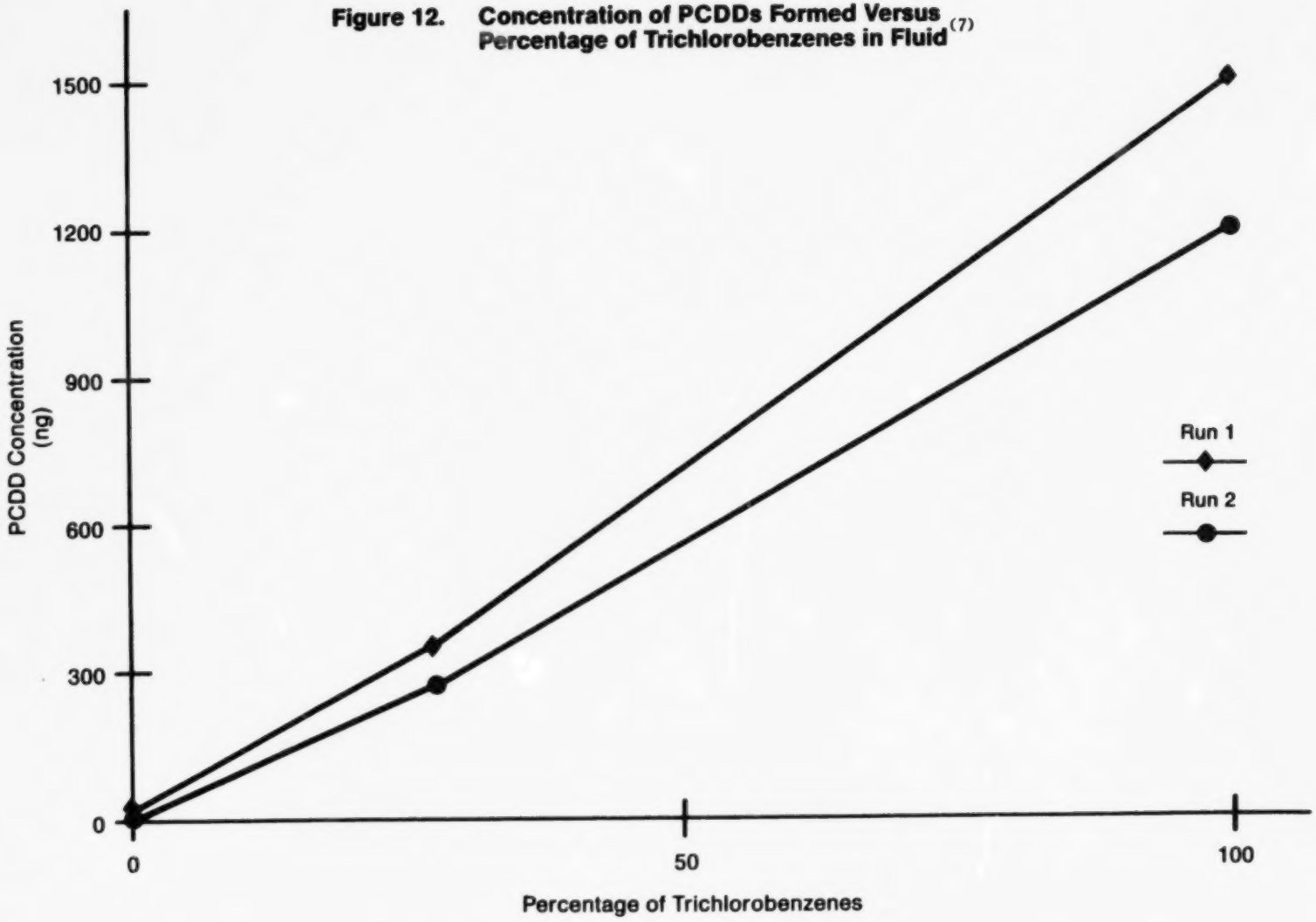


Figure 13. Concentration of PCDDs Formed in Trichlorobenzene-Spiked Fluid by Homolog[7]

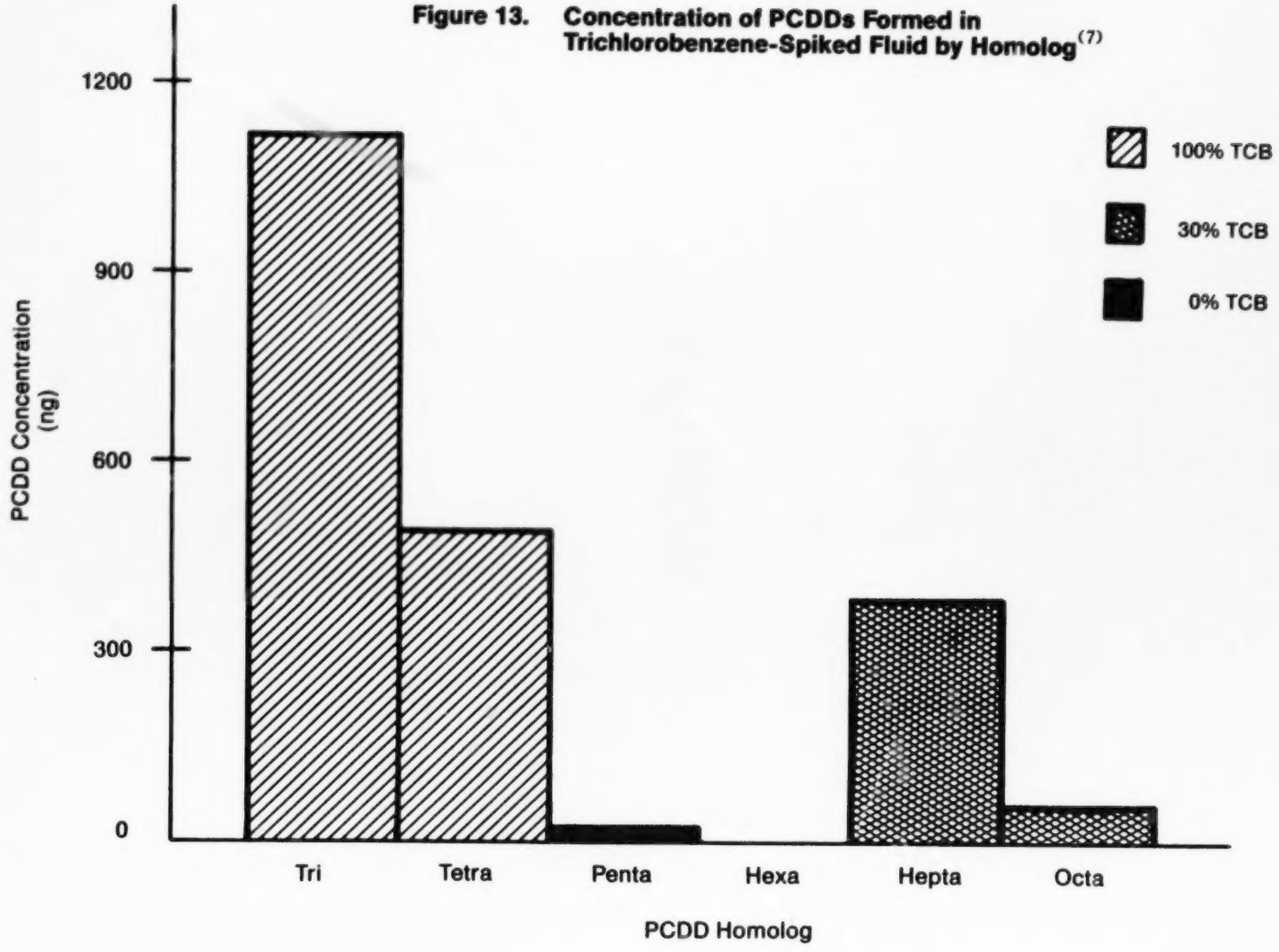


Figure 14. Concentration of PCDDs Formed in Trichlorobenzenes by Homolog[30,36]

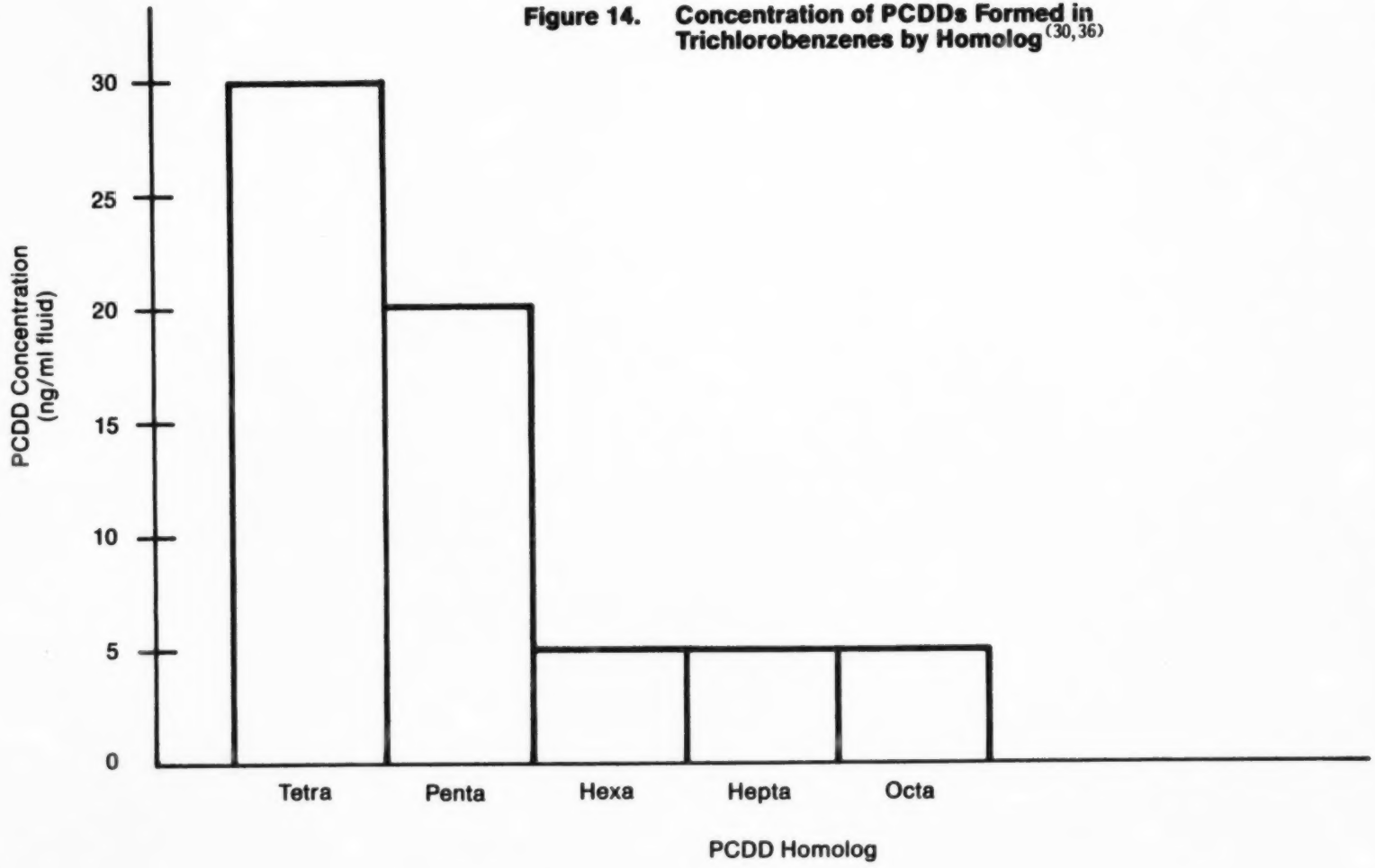
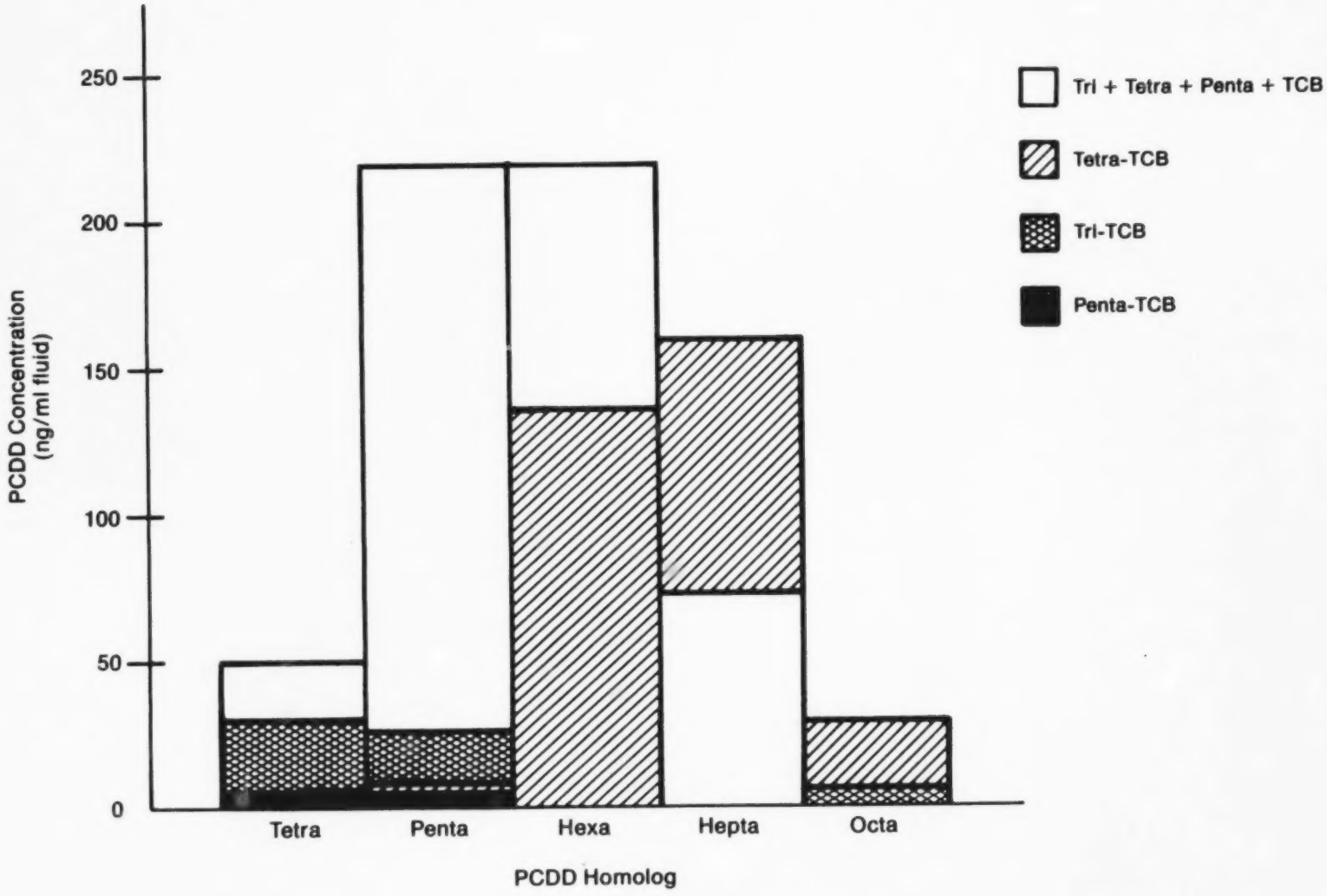


Figure 15. Concentration of PCDDs Formed in Chlorobenzene-Spiked Fluid by Homolog[30,36]



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